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CONTENTS

A Study of a Process for the Production of Dipicrylamine Starting with Benzene
by J. N. Kapoor and J. M. Sarkar 257

Fluidization of By-Product Gypsum Slurry by Sodium Polyphosphates
by Rajendra Singh and A. K. Roy 260

Polarographic Determination of Titanium in Urea
by R. M. Bhatnagar, B. N. Singh and A. K. Roy 264

Desilicification of Raw Waters by the Cold Lime-Magnesia Process Using a Special Grade of Active Magnesia
by G. S. Bhattacharyya, Suresh Singh and B. K. Dutta 268

Corrosion of Refractories by Basic Open Hearth Slags and its Role on the Separation of Ferrophosphorous from the Molten State
by H. Roy, S. K. Sharma, R. Choudhuri and S. Mukherjee 276

Studies on Indian Phosphates—Part I
by R. Choudhuri, A. K. Chakraborty, S. K. Ghosh and K. C. Banerji 285

Determination of Retention Indices of Saturated Hydrocarbons by Graphical Methods
by G. D. Mitra and N. C. Saha 294

Short Communications

A Novel Subtraction Property of Silica Gel for Isoalkyl and Cyclic Paraffins
by N. C. Saha and Samir K. Ghosh 304

Low-Angle X-Ray Study of Humic Acids
by M. Misra, P. K. Pal, C. Aravindakshan and B. K. Banerjee 306

Estimation of Phosphate: A Rapid Polarographic Method
by M. B. Mishra, A. K. Roy Choudhury and B. K. Banerjee 308

Continued on next page

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The opinions expressed by the authors are their own and do not necessarily reflect the views of the Planning and Development Division of the Fertilizer Corporation of India Ltd.

Studies on Broken Valve Plate
by C. Aravindakshan, Ajit Roy, A Sen Gupta, C. V. Srinivasan, S. C. Sinha and P. K. Ghosh 311

Determination of Some Trace Impurities in Ammonium Bicarbonate by Atomic Absorption Spectrophotometry
by R. C. P. Sinha, K. C. Singhal and B. K. Banerjee 313

Estimation of Phosphorus in Rock Phosphate by Flame Emission Technique
by R. M. Sanyal, K. C. Singhal and B. K. Banerjee 316

Infrared Spectra of Chlorapatite
by Vijay Mohan Bhatnagar 319

In the Indian Context

An Economic Evaluation of Nitric Phosphates and Diammonium Phosphate Production
by S. C. Misra, A. K. Bhaduri and R. R. Poricha 321

Letter to the Editor

Rethinking on Special Relativity Theory
by Indu Sekhar Mishra 328

Technical Digests

(*i*) Import Substitution in Fertilizer Industry 330

(*ii*) Carbon Black from Waste Slurry of Petroleum Oil Gasification .. 332

Notes and News 334

News in Brief 347

Statistics 350

A Study of A Process for the Production of Dipicrylamine Starting With Benzene

By

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The process allowed nitration of chlorobenzene to dinitrochlorobenzene in one step. The product obtained was a mixture of 75 per cent α- plus β- and 25 per cent of γ-dinitrochlorobenzene. A mixture of the three isomers was condensed with aniline at room temperature using aqueous alcoholic solution as a condensing medium. Dinitrodiphenylamine formed was freed of aniline hydrochloride and unreacted aniline by acid wash. The filtrate together with the washings were ammoniated and the liberated aniline after extraction with benzene, was obtained back by fractional distillation. The aqueous layer was evaporated to crystallize out ammonium chloride a side product. Dipicrylamine was obtained from dinitrodiphenylamine by nitrating the latter in two successive stages.

Dipicrylamine (hexanitrodiphenylamine) is a costly organic reagent. It has been successfully tried in this laboratory[1,2] for selective extraction of potassium from saline water concentrates. At present, dipicrylamine is prepared mainly on laboratory scale and is not produced in the country. The known preparative methods[3-6] do not take into account possible economy, which could be effected by reducing the steps involved in the preparation, reuse of the unreacted reactants and utilization of side products obtained in the process. With a view to develop a process for large scale production of dipicrylamine, a study has been made of the following process sequence (Fig. 1), starting from nitration-grade benzene, which is available in the country.

Process Sequence

Preparation of chlorobenzene from nitration-grade benzene* was carried out in the presence of powdered iron catalyst following the usual procedure. A slow stream of chlorine gas was passed through 400 g. of dry nitration grade benzene mixed with 3.2 g. finely divided iron powder taken in a reaction flask, kept at 40°C in a thermostatic water bath. The reaction flask was weighed at intervals, when the increase in weight showed a conversion of 60 per cent of benzene to chlorobenzene, the reaction was stopped, as with further chlorination accumulation of side products would have increased. Unreacted benzene was recovered from the reaction mixture by fractional distillation and was recycled. The residual reaction mixture after neutralization with 5 per cent sodium hydroxide solution and separation from the aqueous layer was fractionally distilled to obtain chlorobenzene fraction boiling between 130-134°C. The total yield of chlorobenzene was about 320 g. After accounting for the benzene recovered, conversion of benzene to chlorobenzene was found to be 80 per cent. Hydrochloric acid generated during the process of chlorination of benzene could be recovered[7,8] by the already established processes.

*Obtained from Sindri coke ovens

Nitration of Chlorobenzene to Dinitrochloro benzene

In order to achieve 96-98 per cent conversion of chlorobenzene to dinitrochlorobenzene, with maximum yield of its α- and β- isomers and least amount of the oily γ- isomer (at room temperature, 28-30°C) in single stage, nitration reaction was carried out under certain strictly adhering conditions. Chlorobenzene was dropwise added to a nitration mixture (38 per cent nitric acid and 48 per cent sulphuric acid) containing sulphuric acid less than what is required to obtain the full value of nitric acid in the system, kept at or below 8°C and under constant stirring. The reaction was allowed to proceed at the said temperature for one hour more. The temperature was then slowly raised to 45°C and reaction

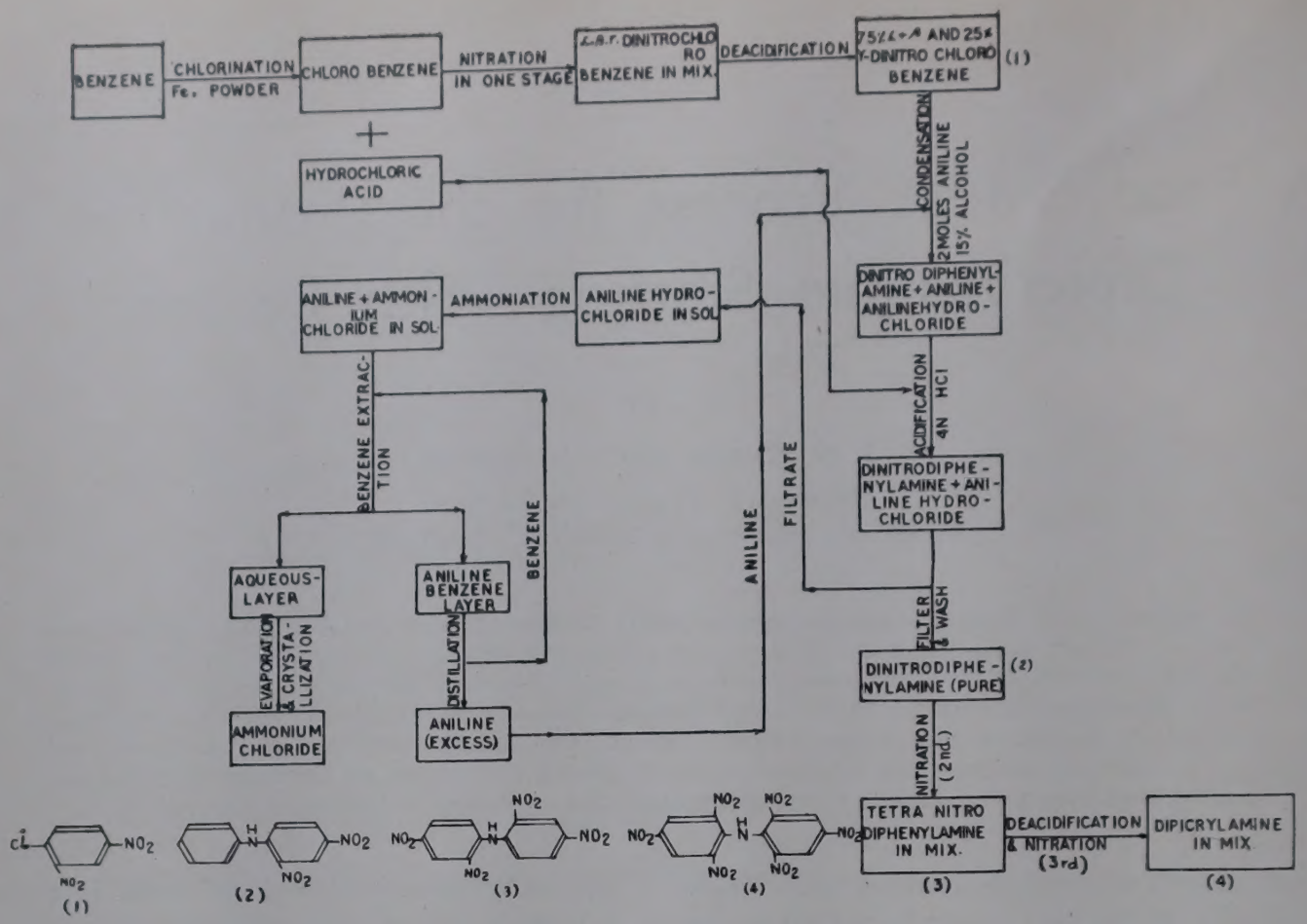

Fig. 1—Flowsheet for the Production of Dipicrylamine.

was further continued for one hour. Thereafter, to obtain the full value of nitric acid in the system more amount of concentrated sulphuric acid was gradually added to the reaction mixture, maintaining the temperature at 45°C.

The reaction mass was finally cooked at 120°C for 40 min. The product on cooling was poured in ice-cold water. Solid α- and β-isomers of dinitrochlorobenzene together with oily γ-isomer were obtained. The isomers were separated and freed from contaminants before drying over in a sulphuric acid bath.

Generally, for a batch of 450 g. of chlorobenzene, 1730 g. of nitration mixture and 700 g. of sulphuric acid were used. The yield of α- and β-isomers was 590-595 g. and that of γ-isomer 190-195 g. which corresponded roughly to 75 per cent α- and β- and 25 per cent γ-isomer. The total yield of dinitrochlorobenzene obtained was 96-98 per cent of the theoretical.

Condensation of Aniline with Dinitrochlorobenzene to Dinitrodiphenylamine

Condensation reaction was carried out with a mixture of α-, β-isomers and γ-isomer of dinitrochlorobenzene taken in the proportions 4:1 with aniline in 15 per cent aqueous alcoholic medium. The quantity of aniline taken was twice the amount required for condensation, the excess required to obtain the maximum condensation of dinitrochlorobenzene to dinitro-diphenylamine. A part of the excess aniline got converted to aniline hydrochloride by the hydrochloric acid liberated in the course of reaction. Presence of alcohol hastened dissolution of more and more aniline as the reaction proceeded and thus, enhanced the rate of reaction. Time taken to obtain the maximum condensation was 2 hours at room temperature (28-30°C). Dinitrodiphenylamine coming out as orange red crystals was contaminated with aniline hydrochloride and aniline. It was filtered and washed free of contaminants by leaching with 4N hydrochloric acid and finally with a little distilled water. Its purity was determined by its melting point (156°C).

Generally, in a batch reaction, 800 g. of dinitrochlorobenzene (mixed isomers) and 732 g. of aniline were taken for condensation in 1600 ml. 15 per cent aqueous alcoholic solution. 1600 ml. 4N hydrochloric acid was required for leaching the product free of con-

taminants. Yield was 980-985 g. of pure dinitrodiphenylamine, corresponding to 95-96 per cent conversion on the basis of dinitrochlorobenzene taken.

The filtrate and washings from the dinitrodiphenylamine separation stage were ammoniated, whereby aniline hydrochloride was decomposed and aniline and ammonium chloride were formed. Aniline was extracted with benzene and was separated from it by fractional distillation. Recovery of aniline amounted to 95 per cent of the excess aniline taken. The aqueous layer contained 16-18 per cent ammonium chloride and was evaporated to dryness to obtain the latter.

Nitration of Dinitrodiphenylamine to Dipicrylamine (hexanitrodiphenylamine)

Nitration of dinitrodiphenylamine to dipicrylamine was carried out in two stages. In the first stage, dinitrodiphenylamine was slowly added to a nitration mixture (40 per cent nitric acid and 19 per cent sulphuric acid), under vigorous stirring, maintaining the temperature of reaction at 25-30°C and continuing the reaction further for 1 hour. Reaction mass was poured in ice-cold water. Tetranitrodiphenylamine separated out in the form of yellow crystals. After filtering, it was washed free of contaminating acids with cold water and finally dried at 100°C.

Generally, in a batch 500 g. dinitrodiphenylamine was reacted with 3590 g. of the nitration mixture. The yield of tetranitrodiphenylamine was 650-660 g., which corresponded to 96-98 per cent on the basis of dinitrodiphenylamine taken for the reaction.

In the second stage, tetranitrodiphenylamine, thus obtained, was uniformly added to a nitration mixture (75 per cent fuming nitric acid and 20 per cent sulphuric acid) under vigorous stirring. Here also the temperature was kept within 25-30°C. The reaction took 90 min. for completion. Golden yellow crystals of dipicrylamine (hexanitrodiphenylamine), which came out, was purified in the same way as tetranitrodiphenylamine.

In a batch, generally 330 g. tetranitrodiphenylamine was reacted with 1670 g. nitration mixture, yield of dipicrylamine (hexanitrodiphenylamine) being 400 g., which corresponded to 96-97 per cent on the basis of tetranitrodiphenylamine taken.

Conclusion

Ultimate yield of dipicrylamine (hexanitrodiphenylamine) from the nitration grade benzene was round about 70 per cent of the theoretical. Main loss of benzene was due to the formation of the side-products during the synthesis of chlorobenzene. Hydrochloric acid requirement in the process for washing purpose can be met mainly by the hydrogen chloride gas evolved during the chlorination of benzene. 95 per cent of the excess aniline being recoverable, the process would require only 5 per cent make-up aniline other than the amount stoichiometrically required for condensation. The full value of ammonia introduced for decomposition of aniline hydrochloride could be obtained back as ammonium chloride. The unreacted nitric acid in the once-used nitration mixture may be recovered back by the well-established process-[7,8] of stripping nitration mixture free of nitric oxide and getting the latter in the form of nitric acid. The dilute sulphuric acid, obtained after such stripping, could be fully utilized for the production of either ammonium sulphate or superphosphate.

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Fluidization of By-Product Gypsum Slurry By Sodium Polyphosphates

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Deflocculation studies on by-product gypsum slurries obtained from wet process phosphoric acid reaction have been made, using different condensed phosphates as the deflocculating agents. Remarkable reduction in apparent viscosities of these by-product gypsum slurries has been attained by the addition of these phosphates. The reduction in viscosity is accompanied by a decrease in the effective size of the particles.

Huge quantities of by-product gypsum are obtained from wet-process phosphoric acid plants throughout the world[1]. In many places this gypsum is slurried with water and sent to disposal dumps, while in others, it is used for making wall-boards and as a retarder in the cement manufacture[2]. In some countries its use has been suggested as a raw material for sulphuric acid, cement clinker being produced as a by-product[3]. In Sindri ammonium sulphate is being prepared on a large scale from natural gypsum, and in the absence of indigenous sources of sulphur the production of ammonium sulphate from by-product gypsum is an attractive proposition, because the sulphate radical is used twice—first in the preparation of phosphoric acid from rock phosphate and then in fixing ammonia as ammonium sulphate[1]. In all these methods for treating by-product gypsum, the material is to be slurried with water in the phosphoric acid plant and pumped to a different location

The economics of the transportation of this by-product gypsum through pipelines will be governed by the viscosity and the percentage of solid present in the slurry[4]. It will be desirable to keep the viscosity low maintaining an increased percentage of solid in the slurry[5]. Thus, the reduction in viscosity of the by-product gypsum slurries will be useful in transporting this material either to plants where it can be subsequently used or even to disposal dumps, through increased efficiency of the pumps, increased solid content in the slurry and lesser sedimentation in the pipelines. The present work was undertaken with this end in view.

In industry, various substances like sodium carbonate,[6,7], sodium hydroxide[8], sodium silicate[9], phosphates[10], calcium chloride, alcohols[11] etc. have been used in deflocculating the slurries of different substances. In the present work it was sought to find out the effectiveness of sodium polyphosphates as deflocculants of gypsum slurries. Greater stress has been laid on the deflocculation of the by-product gypsum slurry by the sodium polyphosphate which is being commercially produced in this laboratory[12]. For comparison, the effects of condensed phosphates obtained from other sources have also been studied.

The by-product gypsum slurries which have to be transported through pipelines in commercial plants will have solid contents in the range of 15 to 40 per cent. In the present work viscosities of slurries have been studied in this range.

Experimental Procedure

The by-product gypsum for the present investigation was obtained from the Jordan variety of rock phosphate (Table 1) by its interaction with sulphuric acid[1].

Slurries of the desired consistencies were prepared from the gypsum by adding requisite amounts of distilled water after making allowance for the free moisture present in the sample. The slurry was taken in a cylindrical pyrex glass vessel and placed in a thermostat controlled at a temperature of $30° \pm 0.1°C$. Viscosity

TABLE 1—CHEMICAL ANALYSES OF THE JORDAN ROCK PHOSPHATE AND THE BY-PRODUCT GYPSUM OBTAINED FROM THE ABOVE ROCK, % BY WT.

Ingredients	Jordan Rock Phosphate	By-Product Gypsum Dried at 45°C
P_2O_5	33.90	1.27
R_2O_3	2.10	0.52
SiO_2+Insoluble	5.18	3.21
CaO	48.00	34.36
SO_3	0.88	44.79
CO_2	3.11	—
MgO	0.03	Traces
NaCl	0.80	—
F_2	4.53	1.42
Moisture	1.26	14.08 (combined water)
Total	99.79	99.65

measurements were made by a Brookfield Synchro-Lectric viscometer model LVT-E, which is a rotating spindle type viscometer having a provision for using a set of spindles which can be made to rotate at eight speeds. During the present work, all the measurements were made at a speed of 30 rpm. The glass stirrer used for stirring the slurry was kept at a suitable speed so as to keep the whole mass moving and the stirrer and viscometer spindle were so arranged that the latter could be set to rotate immediately after stopping the stirrer. The additives to the slurry were in the form of solid and after each addition the stirring was continued and the viscosity measured until the lowest value of viscosity was attained.

For particle size analysis in the sieve-range, wet-sieve analyses of gypsum samples were carried out, while the subsieve analyses were done by the Andreasen pipette method[13] at 35.5°±0.1°C. The suspending fluid used was gypsum-saturated water.

Number average molecular weight and the P_2O_5 content of the sodium polyphosphates used were determined (Table 2). Number average molecular weight, Mn was determined by a relation by Gustavson and Larsson[14] according to which

$$Mn = \frac{20,400}{a}$$

where 'a' is the amount of 0.1N NaOH in ml. required to titrate 1.02 g of sodium polyphosphate.

TABLE 2—NUMBER AVERAGE MOLECULAR WEIGHT AND P_2O_5 CONTENT OF THE POLYPHOSPHATES

Sl. No.	Polyphosphate	Number-Average Molecular Wt. Mn	P_2O_5, %	Na_2SO_4, %	pH of 1% Soln.
1.	Sodium Polyphosphate from Pilot Plant	2700	27.0	59	6.6
2.	Sodium Hexametaphosphate, Star Chemicals, Bombay	630	57.6	—	7.5
3.	Glassy Sodium Polyphosphate prepared from Sodium Dihydrogen Phosphate	5800	69.8	—	5.5

Results and Discussion

From the results given in Table 3 it is evident that the sodium polyphosphate manufactured in the pilot plant

TABLE 3—VISCOSITY REDUCTION OF THE SLURRY DEFLOCCULATED BY SODIUM POLYPHOSPHATE FROM THE PILOT PLANT

15% slurry		20% slurry		25% slurry		30% slurry		35% slurry		40% slurry	
Additive in g. to 100 g. slurry	Viscosity in cp. at 30°C	Additive in g. to 100 g. slurry	Viscosity in cp. at 30°C	Additive in g. to 100 g. slurry	Viscosity in cp. at 30°C	Additive in g. to 100 g. slurry	Viscosity in cp. at 30°C	Additive in g. to 100 g. slurry	Viscosity in cp. at 30°C	Additive in g. to 100 g. slurry	Viscosity in cp. at 30°C
0.0	250	0.0	300	0.0	370	0.0	800	0.0	1750	0.0	2200
0.5	120	0.5	280	1.0	240	1.0	700	1.0	950	1.0	1400
1.0	40	1.0	200	2.0	160	1.5	550	2.0	700	2.0	1000
1.5	15	1.5	90	3.0	100	2.5	340	3.0	500	3.0	840
2.0	10	2.0	70	4.0	90	3.5	270	4.0	360	4.0	720
2.5	10	2.5	55	5.0	80	4.5	170	5.0	300	5.0	600
		3.5	50	6.0	80	5.5	150	6.0	280	6.0	600
		4.0	48			6.5	150	7.0	280		
% Reduction	96		84		80		80		84		73

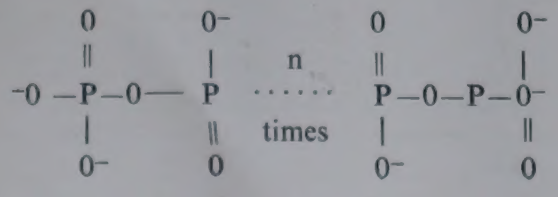
NOTE: The initial pH of the slurry was 3.9 and the final pH after maximum reduction was 5.6.

in this laboratory appreciably lowers the apparent viscosity of the by-product gypsum slurry. This sample contains 27 per cent P_2O_5 and 59 per cent sodium sulphate and the polyphosphate has a number average molecular weight of 2700. The viscosity is reduced in proportion to the amount of polyphosphate added and ultimately attains a value after which there is no further reduction by the addition of extra amount of polyphosphate. The maximum reduction observed is more in the slurries of lower consistencies than in those of higher consistencies, 96 per cent in the 15 per cent slurry and 73 per cent in the 40 per cent slurry. Among the three polyphosphate samples tried, that supplied by Messrs Star Chemicals (Bombay) has the best fluidizing effect. This can be related to its lowest number average molecular weight (Table 4).

TABLE 4—EFFECT OF DIFFERENT POLYPHOSPHATES ON BY-PRODUCT GYPSUM SLURRY (25% SOLID)

Sodium Polyphosphate from Pilot Plant g. to 100 g. slurry	Viscosity at 30°C, cp	Hexametaphosphate (Star Chem.), g. to 100 g. slurry	Viscosity at 30°C, cp	Glassy Polyphosphate, g. to 100 g. slurry	Viscosity at 30°C, cp
0.0	370	0.0	370	0.0	370
1.0	240	0.2	200	0.2	550
2.0	160	0.5	80	0.4	900
3.0	100	0.7	60	0.6	900
4.0	90	1.2	50		
5.0	80	1.4	50		
6.0	80				

It is now believed that the deflocculating efficiency of the condensed phosphates depends largely on their ability to be absorbed on the particle surface, thereby increasing the charge on each particle so as to cause electrostatic repulsion. The anion of polyphosphate bears negative charges and easily forms co-ordinate bonds with electron acceptors such as calcium ions present on the surface of the particles in the slurry[15,16] and thus gets adsorbed, thereby giving negative charge to each particle surface and extending a charged portion of the uncomplexed chain to the medium. The anion of the polyphosphate would be schematically represented as:



All the polyphosphates used in the present study have been shown to be straight-chained by infrared studies[17].

The glassy polyphosphate of high molecular weight used in the present study has actually a flocculating effect and increases the viscosity of the by-product gypsum slurry (Table 4). This flocculating effect may be due to the adsorption of macromolecules on two or more particles at once forming bridges between them and thus wrapping up a bundle of particles[18]. When, however, used in conjunction with sodium sulphate, there is an appreciable reduction in viscosity of the gypsum slurry (Table 5). By itself, sodium sulphate has the effect of increasing the viscosity of the slurry. The synergistic effect of high molecular weight polyphosphate and sodium sulphate is evident in the commercial polyphosphate prepared in this laboratory which contains 59 per cent sodium sulphate and 27 per cent P_2O^5.

TABLE 5—EFFECT OF GLASSY POLYPHOSPHATE ON BY-PRODUCT GYPSUM SLURRY AFTER THE ADDITION OF SODIUM SULPHATE

Additives to 100 g. of 25% slurry, g.			Viscosity at 30°C, cp
	Nil		370
1.0	Sodium sulphate		410
2.0	,,	,,	440
3.0	,,	,,	470
4.0	,,	,,	500
4.0	Sodium Sulphate	+0.2 Glassy Polyphosphate	470
,,		+0.4 ,,	450
,,		+0.8 ,,	400
,,		+1.0 ,,	350
,,		+1.4 ,,	300
,,		+1.6 ,,	250
,,		+1.8 ,,	225

Particle size determinations (Tables 6 and 7) of gypsum from the slurries in presence and absence of polyphosphates show that the viscosity reduction in the slurries by the additives is attended by a general decrease in the effective size of the particles. The effect is more marked in the case of polyphosphate sample from Messrs Star Chemicals, Bombay (Table 7).

Similar observations have been made by other workers[19–21] working with slurries of clay and other materials. The explanation given is that the size distribution of solids in suspension was significant in that a small percentage of fine particles yields a lower viscosity than a suspension of monosized particles. Traxler[22] found that for a given phase-volume ratio of a system, a

TABLE 6—PARTICLE SIZE ANALYSES OF BY-PRODUCT GYPSUM
(Values Represent Cumulative Weight Per cent above Particular Size Range)

Size	Before Deflocculation	After Deflocculation by Polyphosphate From Pilot Plant					
		15% slurry	20% slurry	25% slurry	30% slurry	35% slurry	40% slurry
100 mesh (B.S.S.)	0.74	0.21	0.23	0.19	0.25	0.21	0.38
150 mesh (B.S.S.)	1.06	0.38	0.40	0.34	0.43	0.35	0.54
200 mesh (B.S.S.) (76μ)	1.24	0.59	0.52	0.41	0.51	0.43	0.54
32.6 μ	6.56	2.72	3.12	2.56	4.87	5.21	2.29
22.8 ,,	84.89	79.32	75.82	80.34	86.75	82.47	84.32
18.3 ,,	93.32	84.24	85.14	90.04	89.91	91.35	86.08
12.2 ,,	98.02	89.39	91.23	93.59	90.29	95.46	90.40
7.0 ,,	98.32	95.79	95.34	95.09	95.59	98.71	94.00
4.0 ,,	99.42	98.01	97.89	97.08	97.71	99.07	98.31

TABLE 7—PARTICLE SIZE ANALYSES OF THE GYPSUM SLURRIES (25% SOLID) DEFLOCCULATED BY DIFFERENT POLYPHOSPHATES
(Values Represent Cumulative Weight Per Cent above Particular Size Range)

Size	Before Deflocculation	After Deflocculation	
		Deflocculated by Polyphosphate from Pilot Plant	Deflocculated by Hexametaphosphate from Star Chemicals
100 mesh (B.S.S.)	0.74	0.19	0.22
150 -do-	1.06	0.34	0.40
200 -do- (76μ)	1.24	0.41	0.49
32.6 μ	6.56	2.56	5.83
22.8 ,,	84.89	80.34	49.66
18.3 ,,	93.32	90.04	86.38
12.2 ,,	98.02	93.59	95.46
7.0 ,,	98.32	95.09	98.23
4.0 ,,	99.42	97.08	98.79

decrease in particle size causes a decrease in consistency because (a) particles of various sizes assume a more loosely packed condition than do those of the same size (b) the total volume is less and (c) the volume of the continuous phase separating them is greater.

The fluidization of by-product gypsum slurries by sodium polyphosphates, as shown in the present work, may thus be ascribed to deflocculation by the adsorption of polyphosphate anions on the particles and consequent electrostatic repulsion and the resultant decrease in effective size of the particles.

Conclusion

The apparent viscosity of the by-product gypsum slurries is appreciably and beneficially lowered by the addition of commercial sodium polyphosphates. The fluidization is thought to be brought about by the adsorption of polyphosphate anions on the gypsum crystals by forming co-ordinate complexes with calcium. Simultaneously, there is a decrease in the effective size of the particles. The glassy polyphosphate with higher number average molecular weight has a flocculating effect on the slurry but in conjunction with sodium sulphate it also shows fluidizing effect, thus indicating the synergistic effect of sodium sulphate.

Acknowledgement

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Polarographic Determination of Titanium in Urea

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Polarographic behaviour of Ti^{4+} has been studied with 2M urea, 1M sodium sulphate and 0.5M ammonium sulphate in 3.6N sulphuric acid as the base electrolyte. A well defined wave with $E_{\frac{1}{2}} = -0.260$ volt vs. S. C. E. has been obtained. The slope of linear plot of log i/i_d—i vs. E^1_{de} has been calculated as 0.061 (n=1), showing the system to be reversible[2,3] with single electron reduction of Ti^{4+} to Ti^{3+}. The polarographic method has been applied to determine in urea the amount of titanium which might come from the titanium lining of the urea reactor due to corrosion or erosion.

Titanium is being used as a lining for urea reactors in place of stainless steel. In the urea plant at the Gorakhpur factory of the FCI Ltd., the reactors are made of mild steel lined with titanium. The reactor handles: (a) Ammonia at 105°C and pressure 250 kg./cm²; (b) *Carbon dioxide* at about 140°C, and pressure 250 kg/cm²; (c) *Recycled liquor* at 100°C, whose composition at the inlet is NH_3 39.80, CO_2 29.32, H_2O 21.40, urea 9.26 and biuret 0.22 per cent, and at outlet urea 30.35, NH_3 35.75, CO_2 14.85, H_2O 18.99 and biuret 0.06 per cent at 185°C.

Under these conditions, the titanium lining has been found to be satisfactorily corrosion resistant. Nonetheless, it is desirable to devise some method for the estimation of titanium in the urea stream for plant control purposes.

The present investigation is a polarographic study of the reduction of titanium in urea-sulphuric acid base electrolyte aimed at the determination of insoluble titanium or titania in urea fertilizer which might have got there due to corrosion or erosion of the reactor lining.

Experimental

Polarograms were recorded on a LP-60* self-recording polarograph with a dropping mercury electrode. Glass capillaries with the following characteristics were used throughout the work. All studies were carried out in a H type Novak's cell (Fig. 1). To effect deaeration, nitrogen was bubbled through the cell for 15 min. before each experiment. All the polarographic studies

	m.mg./sec.	t/sec.	h(cm.)	$m^{2/3}t^{1/6}$	
Capillary 1	3.33	2.48	42.7	2.59	(Fig. 2, Tables 1 & 2)
Capillary 2	6.16	3.11	33.7	4.07	(Tables 1 & 3)

*Kovo Instrument Co., Czechoslovakia.

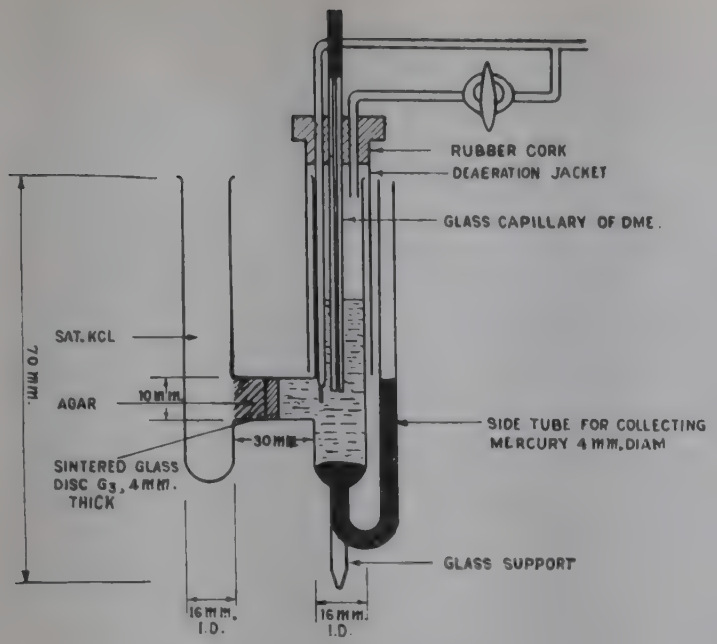

Fig. 1—Novak's Cell.

were carried out at 30°C. Stock solution of titanium was prepared from A. R. potassium titanyl oxalate as given by Vogel[4].

Metallic titanium of 99.1 per cent purity and fertilizer grade urea with 0.6 per cent biuret content was used for the preparation of samples.

Effect of Urea on the Polarographic Behaviour of Ti^{4+} in Concentrated Sulphuric Acid + 1M Sodium Sulphate: Titanium solutions were taken in 100 ml. volumetric flasks. To them, calculated quantities of sodium sulphate, sulphuric acid and urea were added, so that after making up the volume, solution in the flask had 0.005 M Ti^{4+}, 1M sodium sulphate, 3.6N sulphuric acid and varying concentrations, viz. 0, 1M, 2M and 3M, of urea. The polarograms were recorded (Fig. 2).

Effect of Ammonium Sulphate on Polarographic Behaviour of Ti^{4+} in Urea-Sulphuric Acid Base Electrolyte: Solutions were prepared, as in previous para, which after dilution to the mark, had the following compositions (a) 0.005 M Ti^{4+}, 1M sodium sulphate, 3.6N sulphuric acid and 2M urea, (b) 0.005M Ti^{4+}, 1M sodium sulphate, 3.6N sulphuric acid and 0.5 M ammonium sulphate, (c) 0.005 M Ti^{4+}, 1M sodium sulphate, 3.6N sulphuric acid, 2M urea and 0.5M ammonium sulphate Polarograms were recorded.

Effect of Sulphuric Acid Concentration on the Polarographic Behaviour of Ti^{4+} in Urea-Ammonium Sulphate Base Electrolyte: Solutions were prepared as above and after dilution to the mark had the following compositions (indicated in Table 1): (a) 0.005 M Ti^{4+}, 1M sodium sulphate, 2M urea, 0.5 M ammonium sulphate in 1 N sulphuric acid; (b) 0.005 M Ti^{4+}, 1M sodium sulphate, 2M Urea, 0.5 M ammonium sulphate in 2.5 N sulphuric acid; (c) 0.005 M Ti^{4+}, 1M sodium sulphate, 2M urea, 0.5 M ammonium sulphate in 3.6 N sulphuric acid. The polarograms were recorded.

Calibration or Working Graph: To the supporting electrolyte containing 1M sodium sulphate, 2M urea, 0.5M ammonium sulphate and 3.6 N sulphuric acid, different amounts of Ti^{4+} were added. The solutions were made upto the mark and a series of polarograms were recorded. Diffusion currents were calculated and plotted against Ti^{4+} concentration (columns 1 and 2 of Table 3).

Procedure for the Dissolution of Metallic Titanium, Decomposition of Fertilizer Grade Urea and Determination of Insoluble Titanium: 5 g. of fertilizer grade urea containing titanium metal was taken in a Kjeldahl flask and dissolved in 24 ml. of 1:3 sulphuric acid. Titanium is soluble in 1:3 sulphuric acid[5]. The mass was heated gently on a water bath till the metallic titanium came into solution. The solution was cooled and 28 ml. of 50 per cent AnalaR sodium nitrite solution was added dropwise with constant shaking. These quantities of sulphuric acid and sodium nitrite are necessary to decompose 5 g. urea and to give 1 M sodium sulphate in the final solution. The decomposition of urea is necessary because (1) it forms addition compounds with sulphuric acid on heating[6,7], (2) the variation of its biuret

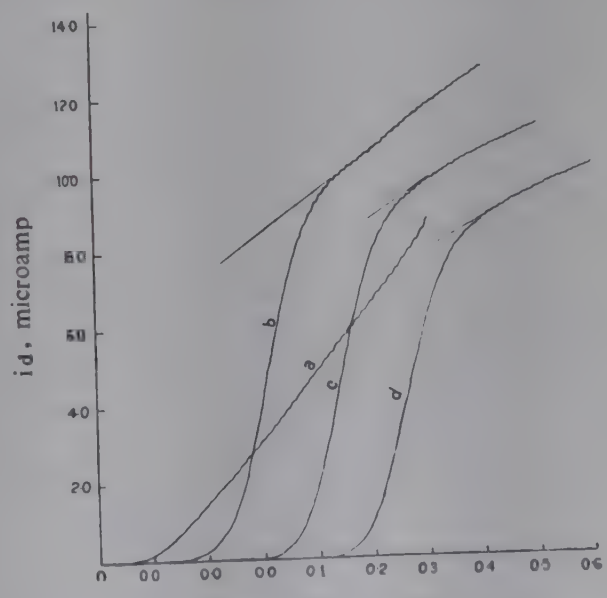

Fig. 2—Polarograms of 5 m MTi^{4+} in Urea Base Electrolyte 1 $MNa_2SO_4 + 3.6\ NH_2SO_4$.

(a) blank, (b) 1 M Urea (c) 2 M Urea and (d) 3 M Urea Capillary 1, Sensitivity 1/200 and Damping 3.

TABLE 1—VALUES OF $E_{\frac{1}{2}}$, i_d, I AND SLOPE FOR Ti^{4+} IN VARIOUS BASE ELECTROLYTE

(Effects)

Sl. No.	Base Electrolyte	$E_{\frac{1}{2}}$ vs. SCE volts	i_d, microamp.	I	Slope Ed_e vs $\log i/i_d-i$	Nature
Effect of Urea						
1.	5mM Ti^{4+}+1M Na_2SO_4+3.6N H_2SO_4	No reduction	—	—	—	—
2.	5mM Ti^{4+}+1M Na_2SO_4+3.6N H_2SO_4+1M Urea	−0.215	8.6	0.65	0.070	Not completely reversible
3.	5mM Ti^{4+}+1M Na_2SO_4+3.6N H_2SO_4+2M Urea	−0.245	8.6	0.66	0.059	Reversible
4.	5mM Ti^{4+}+1M Na_2SO_4+3.6N H_2SO_4+3M Urea	−0.260	8.0	0.62	0.062	-do-
Effect of Ammonium Sulphate						
5.	5mM Ti^{4+}+1M Na_2SO_4+3.6N H_2SO_4+2M Urea	−0.250	8.6	0.66	0.060	Reversible
6.	5mM Ti^{4+}+1M Na_2SO_4+3.6N H_2SO_4+0.5M $(NH_4)_2SO_4$	No reduction	—	—	—	—
7.	5mM Ti^{4+}+1M Na_2SO_4+3.6N H_2SO_4+0.5M $(NH_4)_2SO_4$+2M Urea	−0.260	8.6	0.66	0.061	-do-
Effect of Sulphuric Acid Concentrations						
8.	5mM Ti^{4+}+1M Na_2SO_4+2M Urea +0.5M $(NH_4)_2SO_4$+1N H_2SO_4	No reduction				
9.	5mM Ti^{4+}+1M Na_2SO_4+2M Urea +0.5M $(NH_4)_2SO_4$+2.5N H_2SO_4	−0.275	9.2	0.71	0.065	Not completely reversible
10.	5mM Ti^{4+} +1M Na_2SO_4+2M Urea +0.5M $(NH_4)_2SO_4$+3.6N H_2SO_4	−0.255	8.6	0.66	0.061	Reversible

content above 2% may affect the limiting current of Ti^{4+}, and (3) there is a loss of urea during heating for the dissolution of titanium. A better resolved wave was obtained when experiments were performed after the decomposition of urea.

The solution after the decomposition was transferred to a 100 ml. volumetric flask. Ammonium sulphate, AnalaR urea and sulphuric acid were added so that the final solution had Ti^{4+}, 2M urea, 1M sodium sulphate, 0.5 M ammonium sulphate and 3.6 N sulphuric acid. A polarogram was recorded and Ti^{4+} content was found out from the calibration graph. The results of various analyses are given in Table 3.

TABLE 2—EFFECT OF BIURET CONTENT OF UREA FERTILIZER ON THE VALUES OF $E_{\frac{1}{2}}$, i_d, I AND SLOPE

[Base Electrolyte –2M Urea+1M Na_2SO_4+0.5M $(NH_4)_2SO_4$+3.6N H_2SO_4; *Ti^{4+}*−5.0mM]

(5 g. of urea sample taken and decomposed)

Sl. No.	Biuret, %	$E_{\frac{1}{2}}$ vs. S.C.E. volts	i_d, micro-amp.	I	Slope Ed_e vs. $\log i/i_d-i$	Nature
1.	0.0	−0.250	8.7	0.67	0.061	Reversible
2.	0.5	−0.250	8.6	0.67	0.061	-do-
3.	1.0	−0.250	8.7	0.67	0.061	-do-
4.	1.5	−0.245	8.6	0.66	0.061	-do-
5.	2.0	−0.250	8.6	0.67	0.061	-do-

Effect of Biuret on the Polarographic Behaviour of Ti^{4+} in Urea Base Electrolyte: 5 g. of urea containing varying amounts of biuret and a fixed amount of titanium was treated for the decomposition by the method described above. Polarograms of Ti^{4+} were recorded in the base electrolyte already described. The results are given in Table 2.

Results and Discussion

Ti^{4+} does not give any reduction step in 3.6 N sulphuric acid and 1M sodium sulphate (Fig. 2a). In the presence of urea a reduction step has been seen with a well-defined wave (Figs. 2 a, b & c). The waves with $E_{\frac{1}{2}}$ −0.215, −0.250 and −0.260 volts for 1M, 2M and 3M urea concentrations respectively have been obtained. The value of $E_{\frac{1}{2}}$ is found to change to more negative potentials. This may be due to complex formation between Ti^{4+} and urea and requires further study. The plot of $\log i/i_d-i$ against E_{de} for each curve has been found to be a straight line with slopes 0.070, 0.059 and

TABLE 3—ESTIMATION OF Ti^{4+} IN KNOWN AND UNKNOWN UREA SAMPLES

[Base Electrolyte—2M Urea +1M Na_2SO_4+0.5M $(NH_4)_2SO_4$ in 3.6N H_2SO_4]

(5g. of Urea Sample Taken)

Samples with known Ti^{4+} content		Samples With Unknown Ti^{4+} Content		
Amount of Ti^{4+} /100 ml. base electrolyte, mg.	i_d*, Microamp	Ti^{4+} taken, mg.	Ti^{4+} found polarographically, mg.	% Error
10.0	5.85	2.08	2.06	−0.96
8.0	4.72	6.34	6.31	−0.47
6.0	3.60	4.65	4.60	−1.08
4.0	2.40	1.37	1.34	−2.20
2.0	1.20	1.88	1.86	−1.46
1.75	1.04	0.59	0.59	0.00
1.50	0.90	0.79	0.78	−1.26
1.25	0.76	0.99	1.02	+2.00
1.00	0.60	0.40	0.40	0.00
0.75	0.45	3.17	3.18	+0.30
0.50	0.30	0.59	0.59	0.00
0.25	0.15	0.50	0.51	+2.00

*Values used for calibration graph.

0.062 for 1M, 2M and 3M urea respectively, which indicates that the waves are reversible in 2M and 3M urea. The values of diffusion current constant (I) were calculated as 0.65, 0.66 and 0.62 with respect to urea concentration (Table 1).

Effect of Ammonium Sulphate on Polarographic Behaviour of Ti^{4+} in Sulphuric Acid-Sodium Sulphate -Urea Base Electrolyte: Ammonium sulphate is formed during neutralization of the recycled liquor. Therefore the effect of 0.5M ammonium sulphate has been studied on polarography of Ti^{4+} in 2M urea, 1M sodium sulphate in 3.6 N sulphuric acid. No reduction has been observed when ammonium sulphate is used alone. A well-defined polarogram with $E_{\frac{1}{2}}$ −0.260 volts vs SCE was obtained when mixtures of 0.5M ammonium sulsulphate and 2M urea with 1M sodium sulphate in 3.6N sulphuric acid is used as base electrolyte. The value of slope (Table 1) has been calculated to 0.061 showing the system to be reversible. The value of diffusion current constant (I) remains unaffected and is calculated as 0.66 against 0.68 in 2M urea alone (Table 1).

Effect of Sulphuric Acid Concentration on Polarography of Ti^{4+} in Urea-Ammonium Sulphate-Sodium Sulphate Base Electrolyte: The effect of 1N, 2.5N and 3.6N sulphuric acid have been studied on the polarographic behaviour of Ti^{4+} in 2M urea, 1M sodium sulphate and 0.5 M ammonium sulphate base electrolyte. No reduction has been observed in 1N sulphuric acid (Fig. 4a). Well-defined waves with $E_{\frac{1}{2}}$, −0.275 and 0.255 volts vs. SCE have been obtained in 2.5N and 3.6 N sulphuric acid. At 3.6N sulphuric acid the value of the slope has been calculated as 0.061, showing the system to be completely reversible. The value of $E_{\frac{1}{2}}$, i_d and I are given (Table 1).

Effect of Biuret on the Polarography of Ti^{4+} in Urea-Ammonium Sulphate-Sodium Sulphate in Sulphuric Acid: The fertilizer-grade urea contains varying amounts of biuret, depending upon the condition of manufacture. The effect of biuret upto 2 per cent with respect to urea has been studied after decomposition on the polarographic behaviour of Ti^{4+} in 2M urea, 0.5M ammonium sulphate and 1M sodium sulphate in 3.6N sulphuric acid. From Table 2, it is clear that polarographic behaviour of Ti^{4+} remains unaffected by the amount of biuret (upto 2 per cent). The value of $E_{\frac{1}{2}}$, i_d, I and reversibility have been found to be unaffected by the amount of biuret present.

The results of analysis of titanium content in various urea samples are given in Table 3. The individual errors in the sample, found to be within ± 2.5 per cent, are given in the last column of Table 3. The plot of log i/i_d-i against E_{de} volts for Ti^{4+} in 2M urea, 1M sodium sulphate and 3.6N sulphuric acid is a straight line with slope 0.061 (for 30°C); the value of n was calculated as 1 (theoretical for 25°C, slope = 0.059/n). This shows the system is reversible and confirms the one electron re-reduction of Ti^{4+} to Ti^{3+} according to equation,

$$Ti^{4+} + e \longrightarrow Ti^{3+}.$$

The present polarographic method can give the amount of titanium going with urea or recycled liquor due to corrosion or erosion of the reactor or let-down valve.

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Desilicification of Raw Waters by the Cold Lime-Magnesia Process Using a Special Grade of Active Magnesia

By

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Studies carried out under laboratory conditions on the utilization of an active grade of magnesia, developed in this Division from a particular variety of crude Salem (Madras) magnesite for removing silica from waters in the cold, have shown that the material has a high silica removal efficiency even at ordinary temperatures and may be used along with cold lime softening process without affecting the chemical dosages or the quality of the treated water. The optimum conditions of silica removal may be readily achieved in a cold softener, thereby providing the facilities of combining desilicification with cold softening. Factors, like the effects of concentration of active magnesia, lime, coagulants, preformed sludge, contact time and sludge recirculation on the desilicification have been studied and the data have shown that the silica content of a natural raw water could be reduced easily in the cold from 40 to 0.10 mg./l., maintaining proper cycle of sludge recirculation in 80 min. of retention period, using only 200 mg./l. of active magnesia.

For preventing silica scales on boiler tubes, precipitation process employing magnesium oxide[1,2], dolomitic lime[3], iron or aluminium compounds[4–7] in cold process sludge blanket units, and magnesium oxide or dolomitic lime in hot process units have been studied in the past and some of these were found to be generally satisfactory though some others could not be used in actual practice due to other limitations. By using these processes, it had been possible to reduce the silica concentration of a water to about 3-4 mg./1. in the cold or below 1mg./1 at elevated temperatures. Though with the highly basic ion-exchange resins silica reduction to a low level of 0.01-0.02 mg./1. may be easily achieved, such ion-exchange processes require pretreatment clarification equipment to prevent resin-fouling, especially when the raw water is not entirely clear. Moreover, the strongly basic anion exchanger required for the purpose does not only eliminate silica but other anions as well, thus producing a feed water having an extremely low solid content which is not always required for boiler pressure below 900 psi. and requires costlier sodium hydroxide for regeneration.

The conventional hot magnesia process of silica removal requires a high amount of steam to preheat the water and the steam cost may at times prove expensive.

It was felt that the removal of silica would be econonical if some precipitation process of treatment is developed which would be quite effective at ordinary temperatures and can be employed in conjunction with a cold softening/clarification process depending upon the precipitation reaction. An intensive investigation was undertaken to this effect, and as a result an active form of magnesia was developed in this laboratory by processing a special grade of compact type Salem magnesite under controlled laboratory conditions. The present paper discusses the high silica removal efficiency shown by this especially active magnesia even at ordinary temperatures when used in conjunction with a cold lime softening process. The effects of various factors, e.g. dosages of magnesia, lime, coagulant, preformed sludge, contact time and sludge recirculation, on silica removal have also been studied under laboratory conditions using natural waters.

Experimental Procedure

Cold lime softening-cum-desilicification tests were performed at room temperatures (28-32°C) using 500 ml. of raw water samples taken in 1 l. capacity polythene bottles. The required dosages of chemicals, like lime, coagulants, soda ash, calcium carbonate powder or preformed sludge and active magnesia, were added to these bottles which were subsequently shaken for a definite period on a reciprocal shaking machine at 130 strokes/min. and finally allowed to settle in a quiescent state for a definite time. The conditions of the tests had been incorporated in detail under the different heads studied. The clear supernatants were filtered through Whatman No. I filter paper and the filtrates analysed for pH, alkalinity (P & M), hardness (calcium and total), dissolved solids and silica. All the analyses were done in accordance with the standard methods[8].

Results and Discussion

(*i*) *Analyses of the Raw Waters and Active Magnesia:* Table 1 gives the analyses of the raw waters A, B and C used in this investigation. A was a natural surface water

TABLE 1—ANALYSIS OF RAW WATERS

Constituents	Concentration, mg./1. Raw Water A	Raw Water B	Raw Water C
pH	7.7	7.6	7.8
Phenolphthalein alkalinity as $CaCO_3$	0.0	0.0	0.0
Methyl Orange alkalinity as $CaCO_3$	110	294	146
Calcium Hardness as $CaCO_3$	90	238	118
Magnesium Hardness as $CaCO_3$	66	68	35
Total Hardness as $CaCO_3$	156	306	153
Dissolved Solids as such	256	540	265
Soluble Silica as SiO_2	16	40	20
Turbidity	15	7	4

from the river *Damodar*, whereas B and C were underground waters—the former undiluted and C diluted with an equal volume of distilled water. The chemical analysis of the active magnesia used is given in Table 2.

(*ii*) *Effect of the Active Magnesia Concentration:* With all other chemical additions remaining constant, the dosages of the active magnesia in the raw water samples*

*Natural surface water A was used in all the studies except in those concerned with sludge recirculation where underground waters B and C were used.

TABLE 2—ANALYSIS OF THE ACTIVE MAGNESIA

Constituents	Concentration, %
Moisture	0.40
Carbon Dioxide	8.90
Silica and Insolubles	5.26
Mixed Oxides (R_2O_3)	1.15
Calcium Oxide (CaO)	1.31
Magnesia (MgO)	82.5

were varied from 0 to 320 mg./1. at regular increments. The dosages of chemicals that remained constant in all the samples were as follows: lime as calcium hydroxide 95 mg/1, coagulant (ferric sulphate) 5 mg./1., and calcium carbonate seed crystals 2000 mg./1. The contact period was 80 min. in all cases—60 min. for shaking and 20 for settling. The results show that with increase in the magnesia dosage, silica level in the treated waters decreases (Fig. 1). At about 300 mg./1 of active magnesia concentration, the residual silica was reduced to as low as 0.70 mg./1., but the amount of reduction per part of magnesia was not uniform throughout the entire range of magnesia addition. Successive increases from 60 to 120, 180, 240 and 300 mg./1. in the dosages resulted in a progressive decrease in the quantity of silica removal per part of magnesia from 0.130 to 0.085, 0.065, 0.057 and 0.047 respectively showing the nature as that of an adsorption curve (Fig. 1).

(*iii*) *Effect of Contact Time*: The effect of contact time on silica removal was studied at three concentrations, viz. at 80, and 160 mg./1., of active magnesia,

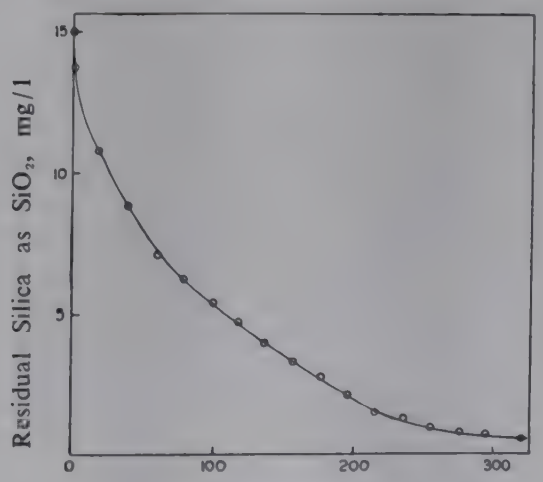
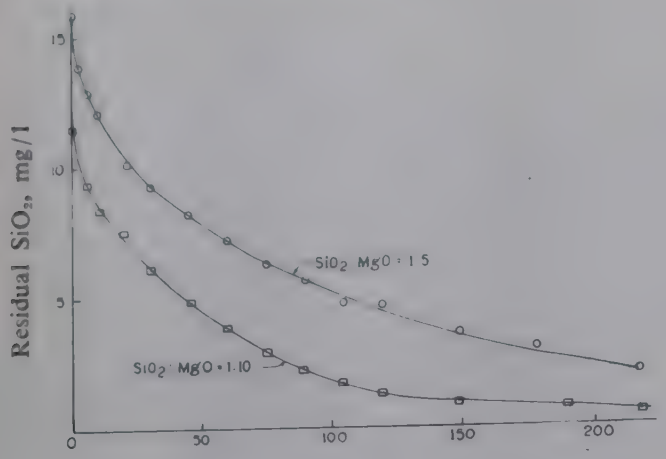


Fig. 1—Effect of Active Magnesia on Desilicification of Raw Water A.

the other chemical additions remaining the same (Fig. 2). The contact time was varied from 0 to 252 min. by



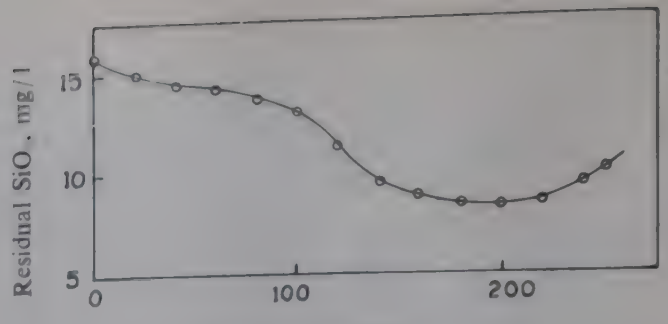
Time, min

Fig. 2—Effect of Time on Desilicification of Raw Water A by Active Magnesia.

changing the shaking period only, time of settling remaining constant at 20 min. The results show that a very high degree of silica removal was achieved at all the active magnesia concentrations by allowing sufficient time for reaction though the percentage silica removal for a particular contact time was higher at higher active magnesia concentrations.

The curves (Fig. 2) show that in the first 30 min. the silica removal was fairly high in all the cases, viz. 41.2 and 61.9 per cent at 80, and 160 mg./1. of active magnesia concentrations respectively. At 60 min. the percentage removals were 55.9, and 75.6 for these concentrations of magnesia which show an increase of 14-16 per cent only in the next 30 min. On further increase in the contact time, the rate of removal was further lowered especially when the active magnesia concentration was reasonably high.

(*iv*) *Effect of Lime:* To study the effect of basic lime softening reactions on silica removal, the raw water samples were treated with increasing concentration of lime ranging from 0 to 260 mg./1 (Fig. 3). To facilitate lime softening the only other chemical dosed to all the water samples was 2000 mg./1. of calcium carbonate seed crystals. The contact time was 80 min. as before. It may be seen (Fig. 3) that upto 100 mg./1 of lime addition, there was practically very little removal of silica indicating that lime does not play any significant part in silica removal at lower dosages, especially below those normally required for partial softening which was 95 mg./1. in this case. However, a sharp fall in silica level was noted when the lime dosages were increased to



Lime as $Ca(OH)_2$, mg/l

Fig. 3—Effect of Lime on Desilicification of Raw Water A.

100-140 mg./1. after which further increase in lime upto 200 mg./1. did not give any appreciable reduction of silica. The increase of lime above 220 mg./1. affected silica removal adversely probably causing resolution of some silica.

The sharp fall in silica level at 100-140 mg./1. of lime was the result of appreciable precipitation of magnesium hydroxide, whereas the slight reduction in the silica content at 0 to 100 mg./1. may be ascribed to an incidental or accidental mechanical dragging of some silica by the precipitated calcium carbonate.

(*v*) *Effect of Coagulants:* The common coagulants, like ferrous sulphate, ferric sulphate and aluminium compounds, have some value for silica removal under controlled conditions[5,7] although their use solely for this purpose usually introduces other factors which make the process inoperative from a practical standpoint. But it was felt that in comparatively much smaller dosages as practised in a cold lime-magnesia softener, these coagulants would not introduce these adverse factors and be rather beneficial.

To evaluate the silica removal potential of these coagulants in the cold lime-magnesia process, the raw water samples were softened-cum-desilicified under conditions where the type of the coagulants was the only variable. The results (Table 3) show that all these common coagulants help the cold lime-magnesia process to different degrees. Whereas the degree of silica removal achieved by 80 mg./1. of the active magnesia without coagulant was 60 per cent, it increased to 69-78 per cent with 20 mg./1. of the coagulant. Iron compounds gave better performance than aluminium compounds.

(*vi*) *Effect of Coagulant Concentration*: The raw water samples were dosed with 80 mg./1. of the active magnesia and 2000 mg./1. of calcium carbonate seed

TABLE 3—EFFECTS OF DIFFERENT COAGULANTS ON COLD LIME-MAGNESIA PROCESS OF SILICA REMOVAL

Sample No.	Type of Coagulant	Chemicals Dosed, mg./l.					Initial Silica in Raw Water Samples as SiO_2	Final Silica in Treated Water samples as SiO_2	Amount of Silica Removed mg./l.	Silica Removal, %
		Lime as $Ca(OH)_2$	Soda Ash as Na_2CO_3	Active Magnesia as MgO	Calcium Carbonate powder	Coagulant as such				
1.	None	95	10	80	2000	0.0	16	6.4	9.6	60
2.	Ferrous sulphate [$FeSO_4$ 7 H_2O]	,,	,,	,,	,,	20.0	,,	4.0	12	75
3.	Ferric sulphate [$Fe_2(SO_4)_3$)]	,,	,,	,,	,,	20.0	,,	3.5	12.5	78
4.	Alum. [$Al_2(SO_4)_3$ $16H_2O$]	,,	,,	,,	,,	20.0	,,	4.6	11.4	71
5.	Sodium Aluminate	,,	,,	,,	,,	20.0	,,	5.0	11.0	69

crystals but with a variable coagulant (ferric sulphate) concentration ranging between 0 and 80 mg./1. An in-increase in coagulant concentration necessitated a corresponding increase in lime and soda ash dosages to maintain the proper conditions of softening and desilicification. The results (Table 4) show that the increase in coagulant dosages from 0 to 20 mg./1., improved the silica removal from 60 to 77.8 per cent but further increase did not show much beneficial effect.

(*vii*) *Effect of Preformed Sludge Concentration:* As silica removal by the cold lime-magnesia process corresponds more with the principle of adsorption than a stoichiometric chemical action, it was expected that concentration of the preformed sludge—formed by the adsorption of silica on magnesia surfaces—would play a vital role in the desilicification process. For this study, all the physical and chemical parameters of the tests, except the sludge concentrations, were kept constant. The preformed magnesia sludge concentration in the raw water samples were varied from 0 to 4500 mg./1. (dry weight) (Table 5). The freshly settled sludge, obtained from a previous set of experiments under identical conditions but without using any magnesia sludge, was centrifuged and washed with silica-free distilled water before using it as a slurry.

It may be noted that with increase in sludge concentration the percentage silica removal increases (Table 5). Whereas without using the preformed sludge silica removal was 62.8 per cent with 80 mg./1. of the active magnesia by using 4500 mg./1. of the former keeping

TABLE 4—EFFECT OF INCREASING CONCENTRATIONS OF COAGULANT ON DESILICIFICATION BY THE COLD LIME-MAGNESIA PROCESS

Sample No.	Chemicals Dosed, mg./l.					Dosage of Ferric Sulphate [$Fe_2(SO_4)_3$] mg./l.	pH of the Treated Water	Initial Silica Content of the Water as SiO_2, mg/l.	Final Silica Content of the Treated Water as SiO_2, mg/l.	Amounts of Silica Removed as SiO_2, mg./l.	Silica Removal, %
	Lime as $Ca(OH)_2$	Soda Ash as Na_2CO_3	Active Magnesia as MgO	Calcium Carbonate Powder	Preformed Sludge						
1.	90	0.0	80	2000	0.0	0.0	10.1	16.0	6.4	9.6	60
2.	95	4.0	80	2000	0.0	5.0	10.0	16.0	6.0	10.0	62.8
3.	101	8.0	80	2000	0.0	10.0	10.1	16.0	4.8	11.2	70.0
4.	107	12.0	80	2000	0.0	15.0	10.0	16.0	4.0	12.0	74.3
5.	112	16.0	80	2000	0.0	20.0	10.15	16.0	3.5	12.5	78
6.	118	20.0	80	2000	0.0	25.0	10.0	16.0	4.1	11.9	74.3
7.	123	24.0	80	2000	0.0	30.0	10.1	16.0	4.4	11.6	72.8
8.	134	32.0	80	2000	0.0	40.0	10.0	16.0	3.0	13.0	81.4
9.	178	64.0	80	2000	0.0	80.0	10.1	16.0	2.8	13.2	82.8

TABLE 5—EFFECT OF PREFORMED SLUDGE ON SILICA REMOVAL BY THE COLD LIME-MAGNESIA PROCESS

Sample No.	Chemicals Dosed, mg./l.					Preformed Sludge Concentration mg./l. of dry wt.	Treated Water Analysis					Silica Removal %
	Lime as $Ca(OH)_2$	Soda Ash as Na_2CO_3	Active Magnesia as MgO	Ferric Sulphate as such	Calcium Carbonate Powder		Alkalinity as $CaCO_3$, mg./l.	Calcium Hardness as $CaCO_3$, mg./l.	Magnesium Hardness as $CaCO_3$, mg./l.	pH	Silica as SiO_2 mg./l.	
1.	95	4.0	80	5	2000	0.0	76	30	83	10.2	6.0	62.8
2.	95	4.0	80	5	0.0	750	72	33	86	10.2	5.2	67.5
3.	95	4.0	80	5	0.0	1500	68	32	78	10.1	4.6	71.2
4.	95	4.0	80	5	0.0	2250	67	34	76	10.15	4.0	75.0
5.	95	4.0	80	5	0.0	3000	66	34	81	10.2	3.2	80.0
6.	95	4.0	80	5	0.0	3750	68	31	76	10.2	2.6	83.7
7.	95	4.0	80	5	0.0	4500	62	34	84	10.1	1.3	91.8

magnesia content the same the removal was as high as 91.8 per cent, thereby raising the efficiency of active magnesia to about 46 per cent.

(*viii*) *Effect of Preformed Sludge Recirculations*: As the beneficial effect of the preformed sludge is generally obtained in actual plant operation by maintaining proper cycles of sludge recirculation or otherwise, a study was made on silica removal by the active magnesia at different cycles of sludge recirculation using raw waters B and C.

Silica removals at various cycles of sludge recirculation were determined at two different dosages of active magnesia using two different retention periods. The zero cycle of the sludge recirculation means when no amount of preformed sludge was used. It was initiated by treating the raw water samples with lime (235 and 130 mg./l. for raw waters B and C respectively), ferrous sulphate (20 mg./l. for both the waters), calcium carbonate powder (2000 mg./l. for both) and active magnesia (200 and 300 mg./l. for B and 100 and 150 mg./l. for C). The two different retention periods were 50 and 80 min. respectively, the time for plain settling being 20 min in both the cases. The sludge formed in the zero cycle was centrifuged, washed and made into a slurry of suitable concentration for use in the next cycle.

The samples of the original raw waters were then treated in identical manner with exactly the same dosages of chemicals, except calcium carbonate which was replaced by 2000 mg./l. (as dry weight) of the sludge formed in the previous operation viz. in the zero cycle. This step of treatment would be termed as the first cycle of sludge recirculation.

A similar treatment of the original raw waters but using 2000 mg./l of sludge from the first cycle formed the second cycle of sludge recirculation. In the third cycle, sludge from the second cycle was used, other additions remaining the same. The data are presented in Tables 6-8b.

Tables 6 and 7 give the silica removal-cum-softening data obtained with raw water B at 200 mg./l. and 300 mg./l. of active magnesia concentration respectively.

These data (Tables 6 & 7) show that percentage silica removal as well as the efficiency of the active magnesia increased with increasing cycles of sludge recirculation. The percentage silica removal and silica removal efficiency were as high as 98.6 and 0.197 respectively, whereas the residual silica in the treated water reached a low value of 0.55 mg./l. in 80 min. of retention time by a proper control of sludge recycling at a magnesia concentration of 200 mg./l. (Table 6).

At magnesia concentration of 300 mg./l., silica in the treated water was as low as 0.10 mg./l. while the percentage silica removal recorded was 99.7. These values were obtained in 80 min. of total retention time with the second cycle of sludge recirculation. But the silica removal efficiency achieved at this concentration was much lower, viz. 0.133 only (Table 7).

The beneficial action of sludge recirculation on cold lime-magnesia process is also evident from similar experiments with raw water C (Tables 8a & 8b). With increase in the cycles of sludge recirculation both the percentage silica removal and efficiency of the magnesia showed an increase. In this case also higher silica removal efficiency was obtained at the lower dosage of magnesia though the percentage silica removal at the zero cycle, i.e. without recirculation, was higher at the higher magnesia dosing.

The percentage silica removal achieved at the zero

TABLE 6—EFFECT OF SLUDGE RECYCLING ON SILICA REMOVAL FROM RAW WATER B BY THE COLD LIME-MAGNESIA PROCESS AT 200 mg./l. OF THE ACTIVE MAGNESIA DOSAGE

1. *With 50 min. total retention time (30 min. for shaking and 20 min. for settling)*

Treatment Cycle No.	Type of Raw Water used	Chemicals Dosed, mg./l.					Treated Water Analysis								Silica Removal %	Efficiency of the Active Magnesia (SiO_2/MgO)
		Lime as $Ca(OH)_2$	Ferrous Sulphate as $FeSO_4 7H_2O$	Calcium Carbonate Powder	Preformed Settled Sludge, as such dry wt.	Active Magnesia as MgO	pH	Phenolphthalein Alkalinity as $CaCO_3$ mg./l.	Methyl Orange Alkalinity as $CaCO_3$ mg./l.	Calcium Hardness as $CaCO_3$ mg./l.	Magnesium Hardness as $CaCO_3$ mg./l.	Total Hardness as $CaCO_3$ mg./l.	Dissolved Solids, mg./l.	Silica as SiO_2 mg./l.		
Zero	B	235	20	2000	0.0	200	10.0	39	62	20	51	71	201	9.5	76.2	0.152
1st	,,	,,	,,	0.0	2000	,,	9.9	40	64	21	51	72	200	3.5	91.2	0.182
2nd	,,	,,	,,	0.0	2000	,,	9.9	40	62	22	50	72	198	2.0	95.0	0.190
3rd	,,	,,	,,	0.0	2000	,,	10.1	40	63	21	52	73	190	1.4	96.5	0.193
2. *With 80 min. total retention time (60 min. for shaking and 20 min. for settling)*																
Zero	B	235	20	2000	0.0	200	10.0	35	62	20	52	72	202	4.8	88.0	0.176
1st	,,	,,	,,	0.0	2000	,,	9.9	38	63	21	52	73	200	2.0	95.0	0.190
2nd	,,	,,	,,	0.0	2000	,,	10.0	40	62	19	50	69	198	0.75	98.1	0.196
3rd	,,	,,	,,	0.0	2000	,,	10.2	41	62	18	51	69	192	0.55	98.6	0.197

TABLE 7—EFFECT OF SLUDGE RECYCLING ON SILICA REMOVAL FROM RAW WATER B BY THE COLD LIME-MAGNESIA PROCESS AT 300 mg./l. OF THE ACTIVE MAGNESIA DOSAGE

1. *With 50 min. total rettntion time (30 min. for shaking and 20 min for setting)*

Treatment Cycle No.	Type of Raw Water used	Dosing of Chemical mg./l.					pH	Treated Water Analysis								Silica Removal per part of Active Magnesia (SiO_2/MgO)
		Lime as $Ca(OH)_2$	Ferrous Sulphate as $FeSO_4 7H_2O$	Calcium Carbonate Powder as such	Preformed Settled Sludge as such dry weight	Active Magnesia as MgO		Phenol *phthlein* alkalinity as $CaCO_3$, mg./l.	Methyl Orange Alkalinity as $CaCO_3$, mg./l.	Calcium Hardness as $CaCO_3$, mg./l.	Magnesium Hardness as $CaCO_3$, mg./l.	Total Hardness $CaCO_3$, mg./l.	Dissolved Solids, mg./l.	Silica as SiO_2, mg./l.	Silica Removal, %	
Zero	B	235	20	2000	0.0	300	9.9	46	87	22	73	95	206	6.1	84.7	0.113
1st	,,	,,	,,	0.0	2000	,,	10.1	46	82	22	70	92	202	2.8	93	0.124
2nd	,,	,,	,,	0.0	2000	,,	10.2	48	75	20	63	83	210	0.65	98.4	0.131
3rd	,,	,,	,,	0.0	2000	,,	10.0	50	70	20	58	78	200	0.65	98.4	0.131
2. *With 80 min. total retention time (60 min. for shaking and 20 min. for settling)*																
Zero	B	235	20	2000	0.0	300	10.0	50	83	19	72	91	200	1.85	95.4	0.127
1st	,,	,,	,,	0.0	2000	,,	10.2	48	80	18	72	90	204	0.65	98.4	0.131
2nd	,,	,,	,,	0.0	2000	,,	10.2	45	72	20	62	82	198	0.10	99.7	0.133
3rd	,,	,,	,,	0.0	2000	,,	10.1	46	69	20	57	77	200	0.10	99.7	0.133

TABLE 8a—Effect of Sludge Recycling on Silica Removal from Raw Water C by the Cold Lime-Magnesia Process at 100 mg./l. of the Active Magnesia Dosage

1. *With* 50 *min. of total retention time* (30 *min. shaking and* 20 *min. settling*)

Treatment Cycle No.	Type of Raw Water used	Dosing of Chemical mg./l.					pH	Treated Water Analysis								Silica Removal per part of Active Magnesia (SiO_2/MgO)
		Lime as $Ca(OH)_2$	Ferrous Sulphate as $FeSO_4 7H_2O$	Calcium Carbonate Powder as such	Preformed Settled Sludge as such dry weight	Active Magnesia as MgO		Phenol phthlein alkalinity as $CaCO_3$, mg./l.	Methyl Orange Alkalinity as $CaCO_3$, mg./l.	Calcium Hardness as $CaCO_3$, mg./l.	Magnesium Hardness as CaCO', mg./l.	Total Hardness $CaCO_3$, mg./l.	Dissolved Solids, mg./l.	Silica as SiO_2, mg./l.	Silica Removal, %	
Zero	C	130	20	2000	0.0	100	9.9	45	62	28	41	69	178	8.7	56.5	0.113
1st	,,	,,	,,	0.0	2000	100	9.6	37	50	28	32	60	174	4.5	77.5	0.155
2nd	,,	,,	,,	0.0	2000	100	9.7	35	51	28	30	58	156	3.0	85.0	0.170
3rd	,,	,,	,,	0.0	2000	100	10.1	40	55	30	32	62	158	1.8	91.0	0.182
								2. *With* 80 *min. of total retention time* (60 *min. for shaking and* 20 *min. for settling*)								
Zero	'C'	130	20	2000	0.0	100	9.9	42	56	24	40	64	170	4.8	76.0	0.152
1st	,,	,,	,,	0.0	2000	100	9.6	37	52	24	36	60	168	2.6	87.0	0.174
2nd	,,	,,	,,	0.0	2000	100	9.8	35	50	26	34	60	158	1.0	95.0	0.190
3rd	,,	,,	,,	0.0	2000	100	10.2	41	52	28	32	60	158	0.5	97.5	0.195

TABLE 8b—Effect of Sludge Recycling on Silica Removal from Raw Water C by the Cold Lime-Magnesia Process at 150 mg./l. of the Active Magnesia Dosage

1. *With* 50 *min. total retention time* (30 *min. for shaking and* 20 *min. for settling*)

Treatment Cycle No.	Type of Raw Water used	Dosing of Chemical mg./l.					pH	Treated Water Analysis								Silica Removal per part of Active Magnesia (SiO_2/MgO)
		Lime as $Ca(OH)_2$	Ferrous Sulphate as $FeSO_4 7H_2O$	Calcium Carbonate Powder as such	Performed Settled Sludge as such dry weight	Active Magnesia as MgO		Phenol phthlein alkalinity as $CaCO_3$, mg./l.	Methyl Orange Alkalinity as $CaCO_3$, mg./l.	Calcium Hardness as $CaCO_3$, mg./l.	Magnesium Hardness as $CaCO_3$, mg./l.	Total Hardness $CaCO_3$, mg./l.	Dissolved Solids, mg./l.	Silica as SiO_2, mg./l.	Silica Removal, %	
Zero	'C'	130	20	2000	0.0	150	9.9	42	87	24	48	72	156	4.8	76.0	0.101
1st	,,	,,	,,	0.0	2000	,,	10.1	43	66	25	47	72	146	3.0	85.0	0.113
2nd	,,	,,	,,	0.0	2000	,,	10.1	44	66	24	46	70	160	2.5	87.5	0.117
3rd	,,	,,	,,	0.0	2000	,,	10.2	54	70	25	48	73	158	1.7	91.5	0.122
								2. *With* 80 *min. total retention time* (60 *min. for shaking and* 20 *min. for settling*)								
Zero	'C'	130	20	2000	0.0	150	9.8	41	61	20	48	68	160	2.3	88.5	0.118
1st	,,	,,	,,	0.0	2000	,,	10.1	46	65	22	48	70	152	1.8	91.0	0.121
2nd	,,	,,	,,	0.0	2000	,,	10.2	46	68	22	51	73	165	1.0	95.0	0.127
3rd	,,	,,	,,	0.0	2000	,,	10.2	48	66	23	49	72	157	0.85	95.8	0.128

cycle of sludge recirculation with 150 mg./1. of active magnesia concentration was nearly the same as that obtained at the first cycle with 100 mg./1. of magnesia concentration. These results indicate clearly that desilicification upto a low level of 0.10 mg./1 can easily be achieved in 50-80 min. contact time by using this magnesia, its consumption being very low—5-10 parts for each part of silica removed. The hardness alkalinity and dissolved solids are also removed along with silica.

Conclusion

Active magnesia could bring down the silica content of water much below 1.0 mg./1. in 50-80 min. of contact time under the conditions of a cold lime softener without affecting the dosages of other chemicals or the quality of the treated water. Its consumption was very low, viz. 5-10 parts for each part of silica removed. Data showed that silica removal by this process corresponded more with the principle of adsorption than with any definite stoichiometric chemical reaction and as such recirculation of the preformed sludge, formed by the adsorption of soluble silica on active magnesia surfaces, increased the efficiency of the process. Hardness, alkalinity and dissolved solids were removed along with silica giving the process an advantageous position in industrial water treatment. As the two processes, viz. cold softening and silica removal, are combined into one without affecting the performance of either process, it will give an economical way of silica removal in the cold.

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Corrosion of Refractories by Basic Open Hearth Slags and its Role on the Separation of Ferrophosphorous from the Molten State

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Corrosion behaviour of some acidic and basic type refractories has been studied with particular reference to the separation of ferrophosphorus from lime-doped phosphate-rich open hearth slags. It has been observed that the lime rich slags, when heated to its molten state at about 1450°C, corrodes these refractories. The nature of this corrosion depends upon the structural characteristics of the refractory bricks and affects the development and separation of the ferrophosphorous mass in the slag melt. In acidic refractories, aluminosilicates are rapidly dissolved by the slag and α-Al_2O_3 phase is crystallized out. Under similar conditions, basic refractories are less attacked although forsterite grains in magnesite brick and magnesite chrome brick are dissolved slowly and interaction products like magnesioferrite and dicalcium ferrite are formed in the latter case. The development and separation of ferrophosphorous in these refractories unlike acidic ones is due to the preferential reaction of free lime with slag and its lowering of viscosity which is perhaps caused by the nature and degree of corrosion.

Basic open hearth slags from steel plants are usually associated with phosphates. Attempts have been made to utilize these slags as fertilizer by grinding[1,2]. But grinding methods are uneconomical, as it involves large consumption of energy, which is costly in developing countries like India. In Czechoslovakia powdering of this slag has been effected by a thermal method which eliminates the conventional grinding process[3]. This self-crushing of open hearth slags is possible in cases where dicalcium silicate is one of the constituents. In India, open hearth slags usually do not contain dicalcium silicate. In many of the cases monticelite (CMS) is the principal phase, which can be used to develop dicalcium silicate provided its lime concentration is increased[4]. But lime doping of the slag will eventually increase its basicity and likely to enhance corrosion of most of the refractories usually used in steel plants. Further, there is a possibility of the formation of ferrophosphorus in those slags, particularly in cases where the iron content is high and P_2O_5 content is low, which is usually found in Indian slags. The formation of ferrophosphorus is possible because of the fact that the distribution coefficient of phosphorus is much more for iron and its alloys than for the slag phase[6]. Some studies have been made on the corrosion of acidic and basic refractories by open hearth and other basic slags[7,10]. But very little is known about the corrosion behaviour of these refractories by those slags when doped with lime. Further the role of their interaction on the separation of ferrophosphorus from open hearth slags doped with additives like lime has not so far been studied. Attempts have been made here to study the corrosion behaviour of refractories by lime doped Indian open hearth slags with particular reference to the separation of ferrophosphorus.

Experimental

The chemical composition of the open hearth slag taken for this investigation is given in Table 1A. The slags are in the form of solid lumps whose average size is about an inch and their fluid temperature is 1330°C.

The refractories chosen for making suitable vessels are acidic refractories, like fire brick and natural Assam

TABLE 1A—Chemical Composition of Open Hearth Slag, %

SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MnO	MgO	P_2O_5
17.33	27.94	1.95	0.74	30.07	4.45	12.20	5.20

sillimanite, and basic refractories, like magnesite and magnesite-chrome bricks. Small rectangular blocks were cut into crucible-like vessels so that each can accommodate about 150 g. of slag in molten condition. The physical characteristics and chemical composition of these refractories are shown in Table 1B. It is evident from this table that the fusion temperature of these refractories is well above the fluid temperature of the slag.

TABLE 1B—Physical Characteristics and Chemical Composition of Refractories

Sl. No.	Refractory sample	Chemical Composition, %	Fusion Temperature, °C	Porosity, %
1.	Fire brick	Al_2O_3-42.44 SiO_2 -55.60	1720	25
2.	Sillimanite	SiO_2 -37.1 Al_2O_3-60.9	1860	Negligible
3.	Magnesite	Fe_2O_3- 5.0 SiO_2 - 5.6 MgO -88.0 Cr_2O_3-Nil	>1860	20
4.	Magnesite Chrome	Fe_2O_3- 6.7 SiO_2 - 5.6 MgO -64.66 Cr_2O_3-18.0	>1860	24

Corrosion study of refractory vessels with slag: Each of the refractory vessels containing a mixture of slag and lime stone (80:20) was taken in a carbon resistance furnace and heated to 1450°C for one hour. Impurities in the lime stone (R_2O_3, SiO_2 and MgO) were found to be below 10 per cent. When the heating was over, the vessels were cooled inside the furnace. The time required to attain the room temperature was about 3 hr in each case. The furnace atmosphere was found to be slightly reducing during heating and cooling period. Photographs of the corroded vessles are shown in Fig. 1.

Microscopic Studies: All refractory samples heated to the reaction temperature (except sillimanite) as well as

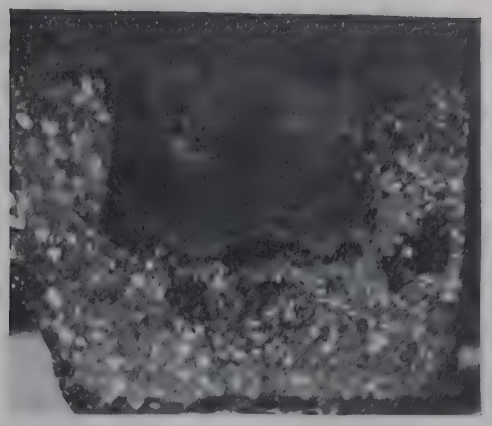


Fig. 1A

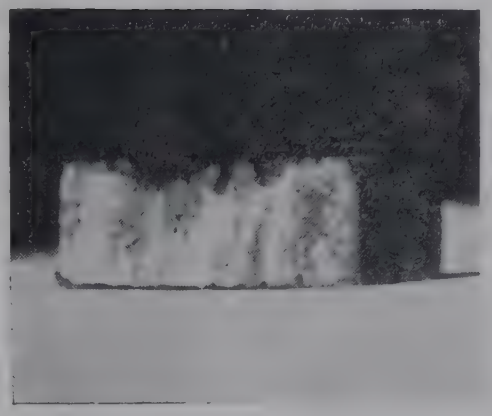


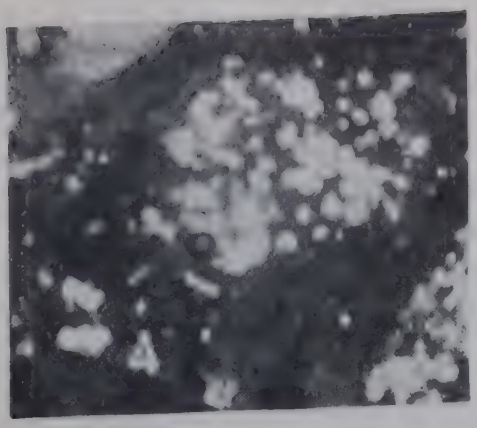
Fig. 1B

Fig. 1C

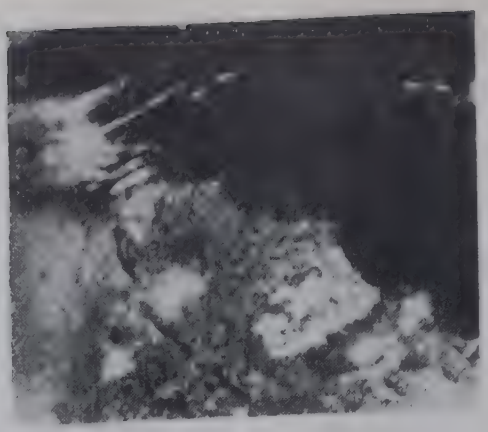
Fig. 1—Corroded Refractory Samples.
(Photographs of sections cut perpendicular to the corroded surface)
A—Firebrick; B—Sillimanite, C—Magnesite Chrome.

their corroded surface were examined under polarising microscope after making their thin sections. Microphotographs are shown in Fig. 2.

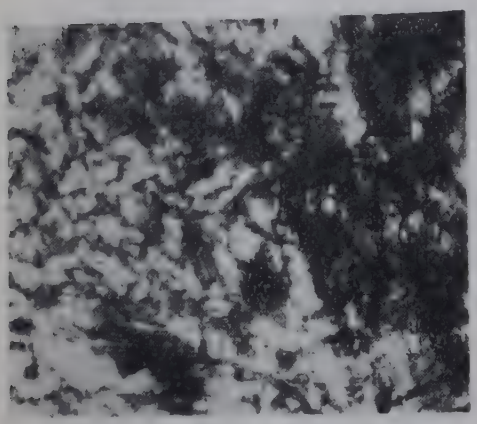
X-ray Analysis: X-ray diffraction patterns of slag, the scrap from the surface and the bulk of the corroded refractory vessels, after heating at 1450°C for one hour,



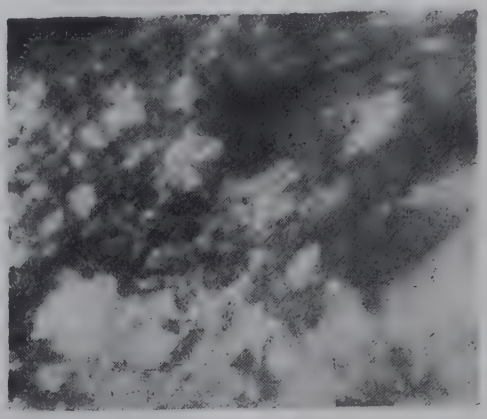
A



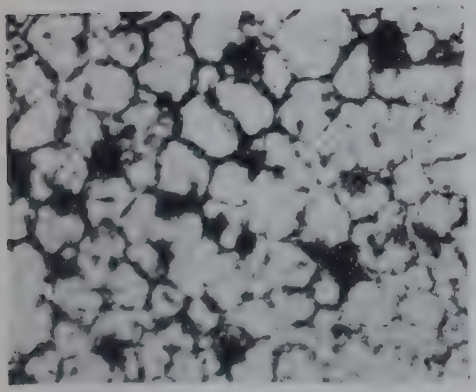
A′



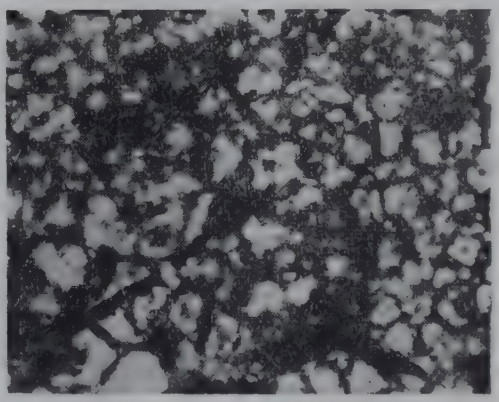
B



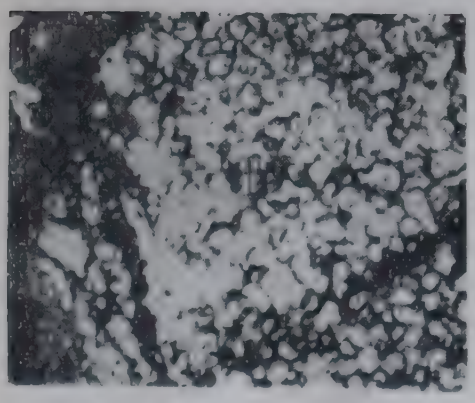
B′



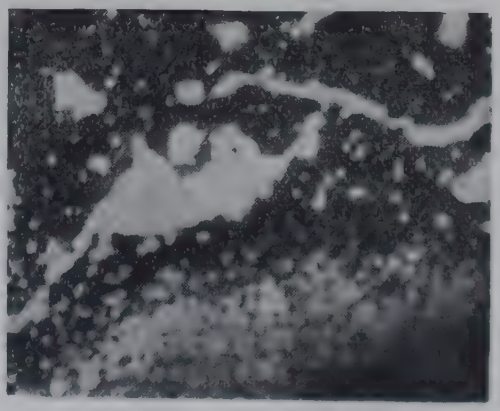
C



C′



D



D′

Fig. 2—Microphotographs of the Thin Section of Refractories and their Corroded Samples.

(with plane polarized light)

A—Quartz and Mullite Grains Embedded in Glassy Mass of Firebrick Refractory. (×84)

A′—Development of Needless near the Ground Glassy Mass of the Firebrick Refractory. (×240)

B—Sillimanite Needles in Sillimanite Blocks. (×84)

B′—Blurring of Sillimanite Needless in Corroded Sillimanite Refractory. (×84)

C—Well-developed Boundary of the Periclase Grains of Magnesite Refractory. (×360)

C′—Diffusion of Slags along the Periclase Boundaries and Slag Attack on Forsterite Grains of Corroded Magnesite Refractory. (×240)

D—Periclase Grains Planked by Dark Chr-omia and Spinel of Magnesite Chrome Refractory. (×240)

D′—Development of Iron Spinel and Dicalcium Ferrite along the Border of Periclase Grains of Corroded Magnesite Chrome Refractory. (×126)

TABLE 2—X-RAY DATA OF REFRACTORIES AND THEIR CORRODED SURFACE HEATED AT 1450°C FOR 1 hr.

Fire brick				Standard Data							
Bulk		Corroded Surface		Mullite[12]		Quartz[12]		Crystabolite[12]		α-Al_2O_3[12]	
d	I	d	I	d	I	d	I	d	I	d	I
5.4	ms	5.40	ms	5.37	70	—	—	—	—	—	—
4.24	w	—	—	—	—	4.26	35	—	—	—	—
4.05	vs	—	—	—	—	—	—	4.04	100	—	—
3.77	vvw	3.76	vvw	3.758	20	—	—	—	—	—	—
—	—	3.48	vw	—	—	—	—	—	—	3.48	60
3.41	ms	3.42	ms	3.418	90	—	—	—	—	—	—
3.39	s	3.395	s	3.383	100	—	—	—	—	3.28	32
3.32	ms	—	—	—	—	3.343	100	—	—	—	—
2.88	mw	2.88	m	2.878	70	—	—	—	—	—	—
2.69	mw	2.69	ms	2.686	80	—	—	—	—	—	—
2.55	s	2.54	ms	2.538	90	—	—	—	—	2.55	85
2.42	w	2.42	w	2.414	60	2.458	12	—	—	—	—
2.28	w	2.28	m	2.289	80	—	—	—	—	—	—
2.20	s	2.20	ms	2.201	90	—	—	—	—	—	—
2.12	mw	2.12	m	2.115	80	2.128	9	—	—	—	—
—	—	2.68	w	—	—	—	—	—	—	2.085	100
1.88	vw	1.88	vw	1.886	50	—	—	—	—	—	—
1.84	vw	1.84	vw	1.839	7)	—	—	—	—	—	—
1.79	vvw	—	—	1.791	3	—	—	—	—	1.741	45
1.71	vvw	1.705	vvw	1.704	60	—	—	—	—	—	—
1.69	vw	1.69	vw	1.693	70	1.672	7	—	—	—	—
1.60	ms	1.595	m	1.596	80	—	—	—	—	1.601	85
1.575	vvw	1.58	vvw	1.573	60	—	—	—	—	—	—
1.52	m	1.52	ms	1.522	90	—	—	—	—	—	—
1.46	vvw	1.458	w	1.459	60	—	—	—	—	—	—
1.44	vvw	1.438	m	1.439	60	—	—	—	—	—	—
1.40	w	1.40	w	1.404	50	—	—	—	—	—	—
—	—	1.37	vvw	—	—	—	—	—	—	1.374	50

d—interlayer spacing Å, I—relative intensity, s—strong, ms—medium strong, m—medium, w—weak, vw—very weak and vvw—very very weak

TABLE 2—(Cont'd)

Sillimanite Corroded Surface		Mullite[13]		Standard Data CMS[14]		$\alpha - Al_2O_3$[12]	
d	I	d	I	d	I	d	I
5.40	mw	5.37	7	—	—	—	—
4.74	vvw	—	—	—	—	—	—
4.57	vvw	4.55	3	—	—	—	—
3.73	vvw	3.725	5	—	—	—	—
3.48	ms	—	—	—	—	3.48	60
3.40	ms	3.401	9	—	—	—	—
3.36	s	3.35	10	—	—	—	—
3.25	vw	—	—	—	—	—	—
3.20	vvw	—	—	—	—	—	—
2.88	w	2.875	7	2.87	7	—	—
2.67	ms	2.669	8	2.65	10	—	—
2.55	s	2.531	9	2.57	5	2.55	85
2.48	vw	—	—	—	—	—	—
2.37	mw	—	—	2.39	5	2.32	32
2.30	vvw	2.999	3	—	—	—	—
2.28	w	2.777	6	—	—	—	—
2.20	s	2.199	10	—	—	—	—
2.11	w	2.108	6	—	—	—	—
2.08	s	2.086	3	—	—	2.085	100
1.88	vvw	1.870	5	1.81	9	—	—
1.83	vvw	1.828	6	—	—	—	—
1.74	ms	—	—	—	—	1.741	45
1.705	vw	1.703	3	—	—	—	—
1.69	w	1.689	6	—	—	—	—
1.68	w	1.677	7	—	—	—	—
1.598	vw	1.594	7	1.59	9	1.601	85
1.568	vw	1.566	6	—	—	—	—
1.518	m	1.516	9	—	—	—	—
1.45	vvw	—	—	—	—	—	—
1.44	m	1.440	7	—	—	—	—
1.40	ms	1.392	5	1.386	6	1.405	35
1.37	ms	—	—	—	—	1.374	50

TABLE 2—(Cont'd)

Magnesite				Standard Data							
Bulk		Corroded Surface		Periclase ASTM 4-0832		Forsterite ASTM 4-0768		Monticellite[14]		Magnesio-ferrite ASTM 1-1114	
d	I	d	I	d	I	d	I	d	I	d	I
5.15	vw	5.05	vw	—	—	5.11	26	—	—	—	—
4.82	vvw	4.84	vvw	—	—	—	—	—	—	4.83	5
4.12	vvw	—	—	—	—	—	—	4.15	3	—	—
3.90	w	—	—	—	—	3.83	69	—	—	—	—
3.73	vw	3.67	vw	—	—	3.73	25	—	—	—	—
3.60	w	3.60	vvw	—	—	—	—	3.62	4	—	—
3.50	vw	—	—	—	—	3.487	21	—	—	—	—
3.13	vw	—	—	—	—	—	—	3.15	2	—	—
3.00	vw	—	—	—	—	3.00	17	—	—	—	—
2.97	m	2.98	ms	—	—	—	—	—	—	2.97	50
2.90	vw	—	—	—	—	—	—	2.87	7	—	—
2.78	vw	—	—	—	—	2.768	53	—	—	—	—
2.63	w	2.679	vvw	—	—	—	—	2.65	10	—	—
2.55	vw	—	—	—	—	—	—	2.67	5	—	—
2.52	w	2.52	m	—	—	2.513	73	—	—	2.53	100
2.47	m	2.47	m	—	—	2.458	100	—	—	—	—
2.425	ms	—	—	2.431	10	—	—	—	—	—	—
2.37	w	—	—	—	—	—	—	2.39	5	—	—
2.35	vvw	—	—	—	—	2.348	9	—	—	—	—
2.31	vvw	—	—	—	—	2.316	9	—	—	—	—
2.28	w	—	—	—	—	2.268	59	—	—	—	—
2.26	vw	—	—	—	—	2.250	33	—	—	—	—
2.16	vw	2.14	vvw	—	—	2.161	15	—	—	—	—
2.10	vs	2.10	s	2.106	100	—	—	—	—	2.09	50
1.80	m	1.83	w	—	—	—	—	1.81	9	—	—
1.755	m	—	—	—	—	1.748	60	—	—	—	—
1.71	vw	1.719	vw	—	—	—	—	1.714	3	1.71	30
1.68	vvw	1.695	w	—	—	1.670	13	—	—	—	—
1.628	vvw	1.621	vw	—	—	1.636	12	—	—	—	—
1.61	vw	1.615	vvw	—	—	1.618	70	1.59	9	1.61	70
1.57	vvw	1.521	ms	—	—	1.572	10	—	—	—	—
1.50	vvw	1.491	w	—	—	1.497	27	1.503	3	—	—
1.485	s	1.48	w	1.489	25	—	—	—	—	1.48	90
1.35	vvw	1.456	vw	—	—	1.351	17	—	—	—	—
—	—	1.330	vvw	—	—	—	—	—	—	—	—
1.267	ms	1.283	vw	1.266	10	—	—	—	—	—	—
1.214	ms	1.216	w	1.212	12	—	—	—	—	—	—

TABLE 2—(Cont'd)

Magnesite chrome				Standard data									
Bulk		Corroded surface		Periclase ASTM 4-0829		Forsterite ASTM 4-0768		Chromespinel ASTM 3-0878		Calcium ferrite[13]		Magnesio-ferrite ASTM 1-1114	
d	I	d	I	d	I	d	I	d	I	d	I	d	I
												4.83	5
—	—	4.85	vw	—	—	—	—	—	—	—	—	—	—
4.80	ms	4.80	w	—	—	—	—	4.82	50	—	—	—	—
3.90	w	—	—	—	—	3.88	69	—	—	—	—	—	—
3.73	vw	—	—	—	—	3.73	25	—	—	—	—	—	—
3.50	vvw	3.50	vvw	—	—	3.487	21	—	—	—	—	—	—
—	—	2.97	m	—	—	—	—	—	—	—	—	2.97	50
2.94	m	2.93	vw	—	—	—	—	2.95	60	—	—	—	—
2.77	vw	2.77	vw	—	—	2.768	30	—	—	2.78	70	—	—
—	—	2.67	w	—	—	—	—	—	—	2.67	100	—	—
—	—	2.53	s	—	—	—	—	—	—	—	—	2.53	100
2.51	s	—	—	—	—	2.513	73	—	—	—	—	—	—
2.50	s	2.50	ms	—	—	—	—	—	—	—	—	—	—
2.46	w	2.45	vvw	—	—	—	—	.252	100	—	—	—	—
2.43	w	2.42	vw	—	—	2.458	100	—	—	—	—	—	—
2.40	vw	—	—	2.431	10	—	—	2.40	10	—	—	—	—
2.27	vvw	—	—	—	—	2.268	59	—	—	—	—	—	—
2.25	vvw	—	—	—	—	2.250	33	—	—	—	—	—	—
2.16	vvw	2.13	vvw	—	—	2.161	15	—	—	—	—	—	—
2.105	vs	2.10	ms	2.106	100	—	—	—	—	—	—	—	—
2.070	ms	2.07	m	—	—	—	—	2.07	70	—	—	—	—
—	—	1.94	vw	—	—	—	—	—	—	1.94	80	—	—
1.750	w	—	—	—	—	1.748	60	—	—	—	—	—	—
—	—	1.714	vw	—	—	—	—	—	—	—	—	1.71	30
1.690	w	—	—	—	—	—	—	1.69	40	—	—	—	—
—	—	1.615	w	—	—	—	—	—	—	—	—	1.61	70
1.595	m	1.592	w	—	—	—	—	1.60	90	—	—	—	—
1.487	ms	1.485	m	1.489	52	—	—	—	—	—	—	1.48	90
1.465	m	1.465	w	—	—	—	—	1.46	90	—	—	—	—
1.400	vvw	—	—	—	—	—	—	1.40	10	—	—	—	—
1.265	vw	1.264	vvw	—	—	—	—	1.26	50	—	—	—	—
1.214	vw	1.215	vw	1.216	12	—	—	—	—	—	—	—	—

were taken by a Guinier camera in a Philips PW 1010 unit using FeKα and CuKα radiation generated at 30 kv, 10 mA and 40 kv 20 mA respectively. The time of exposure was usually 5 hours. X-ray data are given in Tables 2 and 3. FeKα radiation was used in cases where iron content of the samples was found to be high. The phases identified by x-ray and microscopic studies in the bulk of the heated refractories as well as in the corroded surface are shown in Tables 4 and 5. The phases so identified in the bulk of the refractories are in conformity with their chemical composition (Table 1B).

Results

X-ray analysis of the slags reveals that monticelite (CMS), ferrous oxide and α-Fe are the principal phases of this slag (Table 3.). But on addition of limestone to the extent of 20 per cent (10 per cent as CaO) with the slag and heat treatment to 1450°C, a metallic mass consisting of free iron, manganese, magnetite and phosphorus is formed which is separated in the form of small globules in basic refractories only. The analysis of the metallic mass is as follows: Fe as Fe_2O_3-108-P_2O_5 12.5 and Mn 14.6 per cent. Preliminary analysis reveals that the resultant slag is a solid mass and does not contain any dicalcium silicate.

The textures of the bricks have also been observed by microscope. (Fig. 2). In fire brick quartz particles occur as crystalline aggregate and also as tubular crystals. The texture is typically inequigranular where the phenocrystals of quartz and mullite are enveloped in a glassy ground mass, the latter itself forming large circular

TABLE 3—X-RAY DATA OF SLAG SAMPLE

Slag		Standard Data					
		Monticellite[11]		FeO[12]		∝-Fe (ASTM 6-0696)	
d	I	d	I	d	I	d	I
4.16	vw	4.15	30				
3.63	vw	3.62	40				
2.94	vw	—	—				
2.839	w	2.86	70				
2.652	ms	2.65	100				
2.575	w	2.57	50				
2.518	vvw	—	—				
2.481	vvw	—	—	2.475	50		
2.438	vvw	—	—	—	—		
2.386	vw	2.39	50				
2.146	s	—	—	2.145	100		
2.023	vvw					2.03	100
1.807	ms	1.811	90				
1.590	ms	1.59	90				
1.521	m	—	—	1.515	65		
1.428	vvw	1.427	20			1.430	70
1.388	vw	1.386	60				
1.352	vvw	1.355	20				
1.300	w			1.292	20		
1.240	w			1.237	25		
1.170	vvw					1.17	80

pellets. In sillimanite refractory, irregular clusters of well developed fibrous crystals of kyanite, mullite and unaltered sillimanite are densely packed in the body (Fig. 2B). In magnesite brick, periclase occurs as anhydral even sized rounded grains, having occasional cubic cleavage, and isotropic nature. These grains are occasionally clustered together to assume the shape of big rounded pellets which are sometimes rimmed by dark to light brown magnesio-ferrites. The intergranular space is occupied by forsterite crystals (Fig. 2C). In the magnesite chrome refractory, both the larger pellets of chromia with rounded margin and compound pellets of periclase made up with granular periclase are rimmed by iron and chrome spinel (Fig. 2D).

A critical examination of the corroded surface of the refractories reveals that the degree of corrosion is different in different refractories. In fire brick, quartz and cristabolite have been dissolved and a new phase α-Al_2O_3 is crystallized out (Tables 4 & 5). The microscopic examination reveals that the interaction of the melt with these bricks causes both mineralogical and textural changes, and slag appears to have reacted selectively with the border of glassy pellets incorporating quartz and mullite grains resulting in the formation of a new phase which is a needle-shaped mineral (Fig. 2A′). There is also diffusion of slag inside the glassy pellets, where

TABLE 4—PHASES OF REFRACTORIES (HEATED TO 1450°C FOR 1 hr.)

	Fire Brick	Sillimanite	Magnesite	Magnesite Chrome
X-ray study	Mullite, Quartz, & Crystabolite	Sillimanite Kyanite & Mullite*	Periclase, Forsterite, Monticelite (CMS) & Magnesio-ferrite (MF)	Chrome Spinel, Periclase & Forsterite
Microscopic study	Mullite, Quartz & Glass	Sillimanite, Mullite, Kyanite & Iron minerals**	Periclase, Forsterite & Magnesio-ferrite	Chromia, Chrome and Iron spinel, Periclase & Forsterite

*Predominant Constituents in natural Sillimanite (from Ref. 10).
**Constituents in natural Sillimanite.

TABLE 5—PHASES IDENTIFIED IN CORRODED SURFACE OF THE REFRACTORIES

Fire Brick	Sillimanite	Magnesite	Magnesite Chrome
Mullite & α-Al_2O_3	Monticelite (CMS), Mullite & α-Al_2O_3	Periclase & Magnesio-ferrite (MF)	Periclase, Chrome spinel, Calcium Ferrite (C_2F) and Magnesio-ferrite

it attacks the quartz grains. The appearance of α-Al_2O_3 in the surface of the brick indicates a preferential dissolution of SiO_2 from Aluminosilicate. The corrosion effect is maximum in this case, of all the refractories studied (Fig. 1).

The effect of interaction of slag with sillimanite is very conspicuous near the interface and gradually diminishes within the body. Unlike fire brick, only mineralogical change is evident in this brick (Fig. 2B, B′). Further, the appearance of new phases like α-Al_2O_3 indicates that the melt dissolves the surface preferentially like fire brick and α-alumina is crystallized out. The low diffusion of melt in sillimanite body is evidently due to its negligible porosity (Table 1B).

In magnesite brick, the slag has effectively diffused along the interface of the refractory. But the melt attacks preferentially the forsterite grains occurring along the intergranular space (Fig. 2C, C′).

Magnesite chrome refractory appears to have been least affected by the melt (Fig. 1). The only effect that could be seen under microscope is slight darkening of the ground mass as well as of the anisotropic pellets (Figs. 2D, D′). But the shade diminishes imperceptibly within the body with increasing distance from the reaction surface. This shows that there also, the melt has diffused through the body as in magnesite brick, and attacked the forsterite grains. This diffusion is possible because of their high porosity (Table 1B). Further, magnesio-ferrite is formed in this refractory. Along with this there is also an evidence of the formation of dicalcium ferrite in this brick. This compound may be formed as a result of interaction of free lime with iron spinel of the brick, which is present in this refractory.

Discussion

In a reducing atmosphere lower valent iron and manganese oxides are easily reduced. But the fact that separation of ferrophosphorus is observed only in basic bricks from the lime doped slags, indicates that the corrosion plays a vital part in this process. It is evident from the results that the nature of the corrosion of refractories by lime doped open hearth slags depends upon the structural characteristics of refractories. In acidic refractories free lime seems to be rapidly reacted with the SiO_2 of the aluminosilicates rather than with the slag. Unlike this, basic bricks are less attacked by this slag and the major reaction occurs mainly with lime and slag. The preferential interaction of lime with slag in the molten state may be one of the reasons for the rapid reduction of lower valency iron and manganese oxides to their metallic state. The formation of ferrophosphorous compound is possible because the distribution coefficient of phosphorus is higher for iron and its alloys than for the slag phase[6]. The corrosion also affects the separation of this metallic phase from the molten state. According to Kozakevitch[11] et al the phosphated slags with powdered lime are very fluid in molten condition. But with the increase of SiO_2 content the viscosity of the slag melt increases. Contrary to this the effect of MgO and Fe_2O_3 is not so pronounced as of SiO_2[5]. In acidic refractories, the viscosity of the resultant slag melt increases rapidly due to progressive dissolution of silica. Further, it is likely that the melt becomes more viscous due to the presence of α -Al_2O_3 which crystallises out at the operating temperature. In basic bricks there is less corrosion and the chemical constituents that go to the slag melt due to corrosion of bricks are MgO and Fe_2O_3 mainly with little of SiO_2. Eventually the resultant melt is less viscous in basic refractories than in acidic ones. The ferrophosphorous phase is immiscible with the slag in molten state and gets separated easily if the viscosity is low. As such this phase is easily separated in basic bricks where the resultant slag is less viscous.

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Studies on Indian Phosphates—Part I

By

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Rock phosphates from all the Indian deposits discovered so far, viz. from Rajasthan, U. P., Madras, Bihar and Andhra Pradesh, have been studied by thin-section microscopy, infra-red and x-ray diffraction techniques and their physical characteristics determined. The paper also brings out the mode of occurrence of these deposits, their mineralogical association and exploitation feasibilities.

The majority of the phosphatic deposits of the world are of sedimentary origin and supply over 85 per cent of the total phosphate requirement. In India, however, till a few years ago, all the mineral deposits known were of igneous type. Only recently occurrence of some sedimentary phosphatic deposits have been reported by G.S.I., a few of which are worth economic exploitation. Significant deposits have been located in Udaipur, Jaisalmer and Barmer districts of Rajasthan and in Dehra Dun, Pauri and Tehri districts of U.P. The occurrence of phosphotic nodules in Tiruchirapalli district of Madras were also known from earlier times but not considered of economic importance. Amongst the igneous deposits, small scale mining of apatite in Singbhum district of Bihar has been in practice for a pretty long time. Apatite veins of Visakhapatnam district, reported earlier and largely extended recently by F.C.I., are also being mined.

So far no systematic study of Indian rock phosphates has been made. It is well-known that prior to their utilization for large scale manufacture of phosphatic fertilizers, it is essential to consider several individual factors of these deposits apart from their P_2O_5 content such as their physical, chemical and structural characteristics, mining and beneficiation feasibilities etc. The present paper describes some of the studies that have been carried out to examine these aspects. Further work is in progress and will be reported later.

Geological Setting

The Kanpur (24°34′: 73°46′), Maton (24°33′: 73°47′) and Dokan Kotra near Udaipur (24°29′ 45″: 73°43′ 45″) deposits occur in the Aravalli system of pre-Cambrian age[1]. The discovery of these horizons is significant because phosphatic formation belonging to pre-Cambrian age are rare in the world. The other reported occurrence of such phosphatic horizons are of Tzin-Sian and Cayan (China) of Sinian age (youngest unmetamorphosed system of pre-Cambrian age)[2]. The phosphatic materials are associated mainly with dolomitic marble and sometimes with cherty brecciated quartzite belonging to the *Aravalli* series. Close association of stromatolites with phosphatic material is very conspicuous[3].

The deposit reported in Jaisalmer district of Rajasthan belongs to the Birmania formation of Paleozoic age. Here too the phosphatic materials are associated with limestone and chert. The third phosphorite horizon in this region has been discovered by G.S.I. in the Lathi formation of Mesozoic age near Fatehgarh (25°30′: 71°12′), also, in Jaisalmer district. The phosphatic materials are associated mainly with sandstone.

In the large phosphatic deposits of Mussoorie and its neighbouring area, (Dehra Dun, Tehri and Pauri districts)[4], the phosphoria formations are restricted mostly to the lower *Tal* shales near the junction of these with the underlying *Krol* limestone. The beds consist of carbonaceous shales and the slates associated with black cherts in a form, typical of primary bedded phosphate deposit. The lower *Tal* shales and the underlying *Krols* occur in the form of a syncline known as the Mussoorie Synform, the axial trend of which strikes in N50W-S50E direction. The potential phosphate bearing zone covers an area of over 120 square Km

within the Mussoorie synform. One typically identical occurrence of phosphate horizon has also been reported in Nainital area of U.P.[5].

The occurrences of phosphatic nodules of the Uttatur stage of Tiruchirapalli Cretaceous, reported long back[6], are extermely sporadic. Comparatively higher concentration of these nodules could be located in three places, viz. Karai (11°8′: 79°53′), Tirani (11°6′: 79°52′) and Nambakurichi (11°3′: 19°52′).

Apart from the above sedimentary deposits, there are two localities, viz. Singbhum district of Bihar and Vishakapatnam district of Andhra Pradesh, where igneous phosphate deposits have been found. In Singbhum, the apatite occurs as lenses arranged in an *en echelon* pattern which are restricted within the Singbhum shear zone and occupy all along its 60 Km. length extending from Itagar on the west, to Khejurdari on the south-east. The lenses occur in close association with magnetite amidst the biotite chlorite schist. In Kasipatnam-Sitarampuram area of Visakhapatnam the apatite mostly occurs as pure apatite veins of varying thickness ranging from a few centimetres to 7 feet and extending, in a few cases, to nearly 500 feet along the strike direction.

Experimental

Representative samples collected at closely spaced intervals from ten areas covering the localities described above have been exhaustively studied, from which about 120 specimens were subjected to microscopic examination and refractive indices measured by immersion method wherever possible.

Infrared spectra of some 30 specimens of selected variety in the solid phase were analysed by the KBr pellet techniques using a Dual grating Perkin-Elmer Infrared spectrophotometer, model 421. The pellets 13 mm. diam. ×1.0 mm. thick, were prepared following a procedure described earlier[7], and the spectra recorded from 2.5 to 18 microns with scanning speed set to cover the whole range in about 17 minutes.

X-ray diffraction patterns of about 22 specimens were obtained in a Guinear camera with CuKα radiation with nickel filter at 40 KV and 20 mA, giving 6-8 hours of exposure to each sample. The lattice parameters were calculated from the observed diffraction pattern with measurements at maximum accuracy and by referring to hexagonal axes with the following equation:

$$\frac{1}{d^2_{hkl}} = \frac{4}{3}\,\frac{(h^2+hk+k^2)}{a^2} + \frac{l^2}{c^2}$$

which relates the cell parameters to any given interplaner spacing, d, of known Miller indices (hkl). The apatite reflection corresponding to 300, 140, 202, 222 and 402 were used in evaluating the lattice constants.

Mineralogy and Petrography

Thin sections of the Kanpur Maton samples show that the phosphatic materials occur as extremely fine irregular granules cemented by calcareous and cherty material (Fig. 1). The phosphatic granules range in size from 0.03 to 0.06 mm. on an average. However, the average grain size is relatively finer in Maton rock phosphate. Irregular phosphatic algal structures could be seen occurring in association with cherty quartzite (Fig. 2). The phosphatic material is distinctly anisotropic.

Thin sections of *Birmania* phosphates show that the phosphatic materials occur in the form of elliptical ovules (Fig. 3), mainly consisting of collophane with their long axes arranged distinctly parallel to the bedding. The ovules show variable colours like white, pinkish white, dark grey etc. and range in size from 0.1 to 0.5 mm. on an average. These are embedded in a highly calcareous matrix which incorporates angular quartz grains, but at times are so closely spaced as to form pure phosphatic bands alternating with calcareous bands with or without any phosphatic ovules. The collophane ovules are, in a few cases, *rimed* by light coloured fibrous material (Fig. 4) which appears to be dahllite. Sometimes the phosphate pellets show distinct light and dark coloured concentric zones (Fig. 5).

Thin sections of the samples collected from the different localities of Mussoorie and Nainital area show considerable amount of similarity as regards their

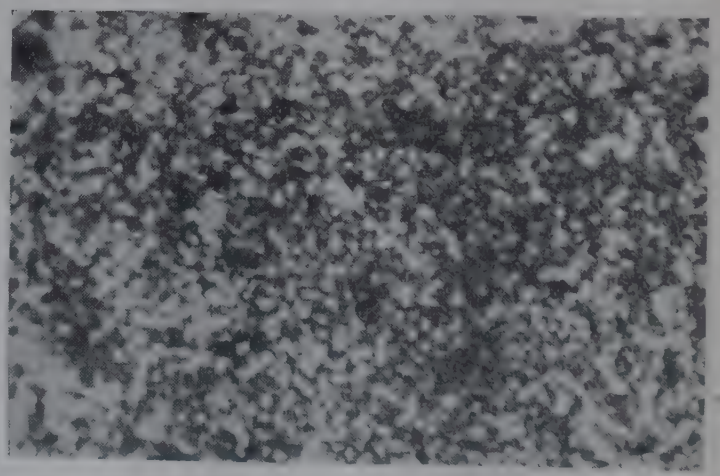

Fig. 1—Granular francolite cemented by cherty and calcareous materials crossed nicol × 475.

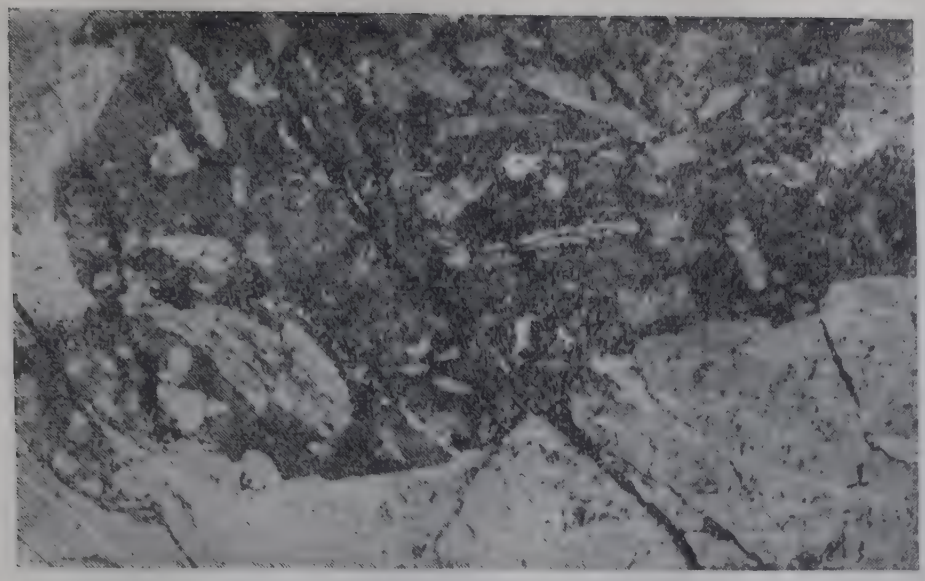

Fig. 2—Irregular algal structure (dark) associated with phosphatic material (grey)—plane pol × 5.

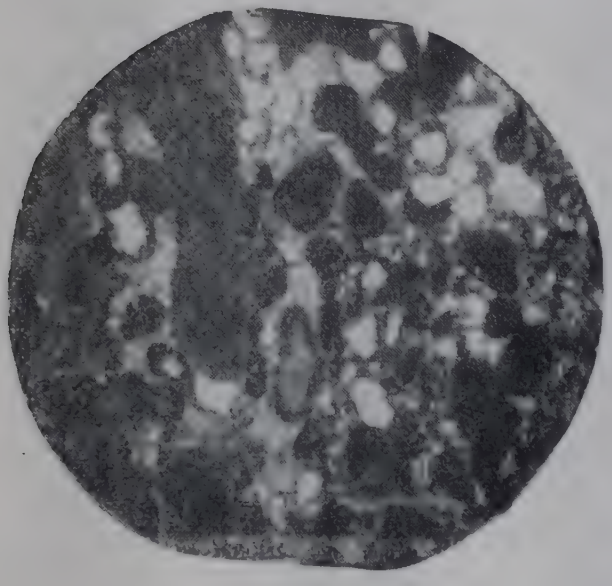

Fig. 3—Light and dark coloured collophane set in a highly calcareous matrix. The elongated black pellet represents coprolite and white angular frangments are quartz plane pol × 90.

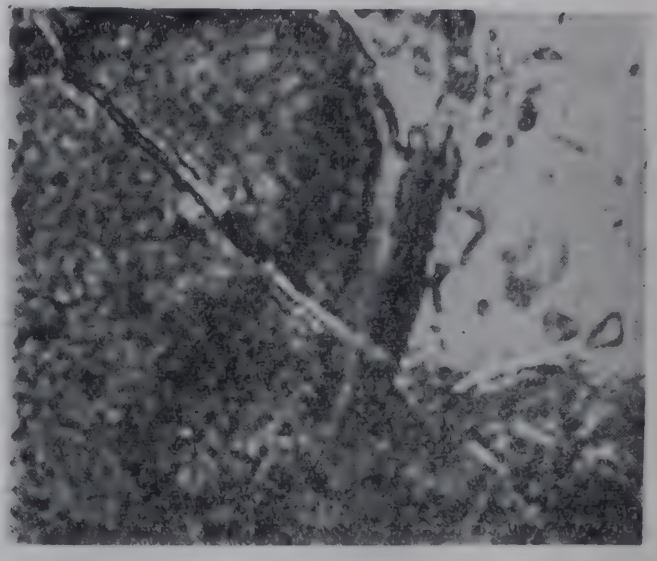

Fig. 4—Collophane ovules rimmed by fibrous dahallite—plane pol × 460.

Fig. 5—Collophane ovules showing light and dark coloured concentric zones—crossed nicol × 180.

mineralogy. However, there is one occurrence (*Paritibba*) in the Mussoorie synform where nodular phosphate could be encountered. The individual nodules range in size, on an average, from 0.1 cm. to 1 cm and mostly elliptical in nature. The nodules are set in a clear and highly calcareous matrix (Fig. 6) assuming the appearance of a typical conglomerate. Microgranular phosphatic materials also form an important constituent of the matrix. Occasionaly the nodules show distinct concentric shells but in most cases they are lacking. The nodules are made up either of extremely fine grained francolite (light coloured) or of collophane (dark coloured) (Fig. 7). The same phosphatic nodules in-

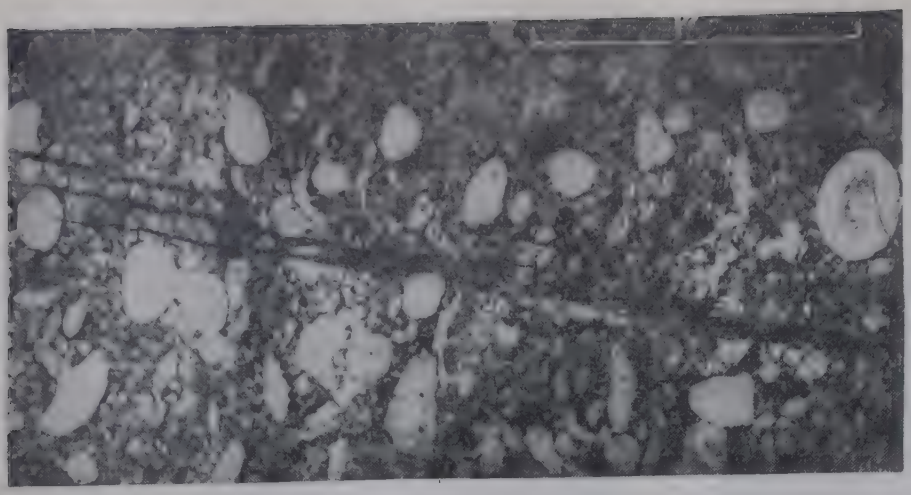

Fig. 6—Nodules of francolite and collophane embedded in a calcareous matrix assuming the appearance of typical conglomerate. Concentric shells could be seen in the biggest nodule— negative print.

Fig. 7—Phosphatic nodules made up of microcrystalline francolite—crossed nicol × 75.

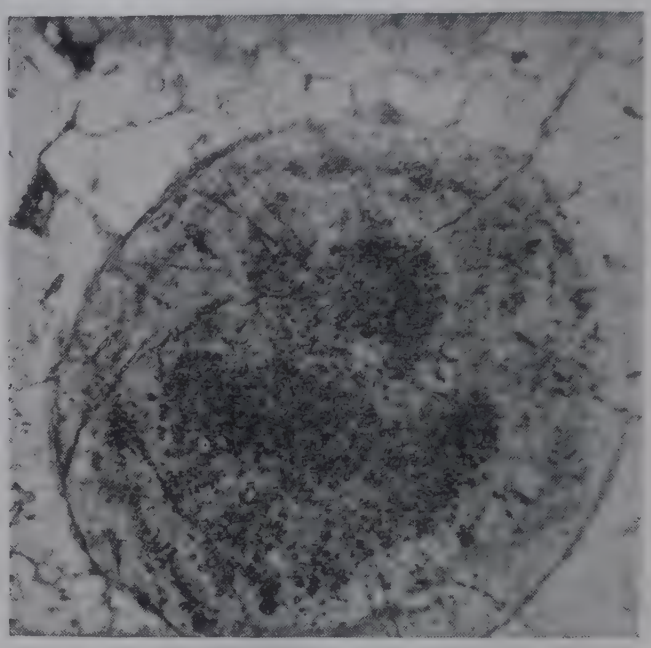

Fig. 8—Francolite nodules incorporating microcrystalline granules of glauconite clustered near the core—plane pol × 75.

corporate green to dark brown microcrystalline rounded grains clustered together near the core of the nodules. These are suspected to be glauconites (Fig. 8). The phosphatic rocks collected from other parts of the Mussoorie synform e.g. Kimoi and Masrana, as well as from Nainital show fine scale banding of relatively pure phosphate alternating with shally bands in which only the sericite could be deciphered. Dark and light coloured pellets of collophane and francolite embedded in a matrix made up of phosphatic and clay material have been found to occur in these areas. The matrix also incorporates angular quartz and feldspar grains. Both dark and light coloured pellets are sometimes encircled by banded and fibrous dahllite (Fig. 9) which mostly occurs as a secondary mineral. Apart from pellets, in a few cases, the angular fragments made up of francolite granules have been found to be set in the same matrix. (Fig. 10). Association of glauconite with Mussoorie and Nainital phosphate is not an uncommon feature (Fig. 11). Thus it will be evident that in the rock samples collected from various localities in the neighbourhood of Mussoorie and Nainital, the phosphatic material appears to occur in three forms namely (a) nodules of collophane and francolite, (b) relatively pure phosphate with fine scale banding, and (c) ovules, pellets and fragments of collophane and francolite.

In the Tiruchirapalli collections of the nodules, collophane is the chief phosphatic constituent. The size of the nodules varies, in general, from 5 to 10 cm, which are highly fractured in nature, and veining of calcite, celestite along these fractures is a very common feature (Fig. 12). The nodules occasionally incorporate fossils

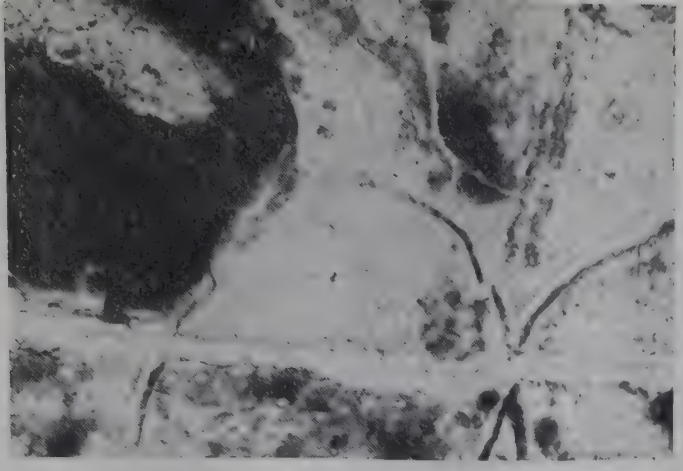

Fig. 9—Both dark and light coloured pellets of collophaneα francolite encircled by fibrous dahallite—plane pol × 150.

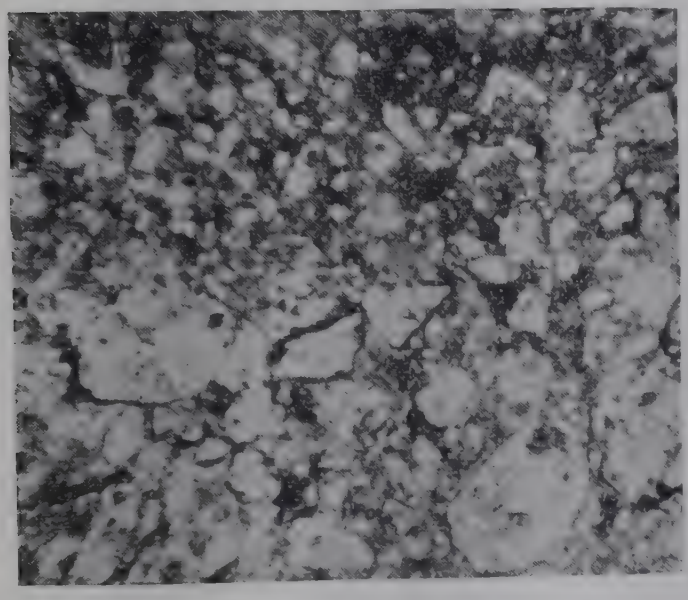

Fig. 10—Fragmental pellets of francolite set in matrix of same—plane pol × 20.

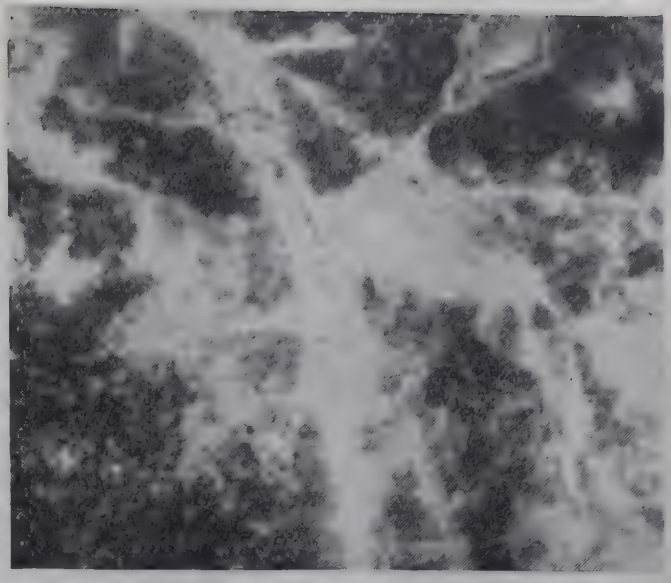

Fig. 11—Glauconite (white) occurring across the pellet of francolite and also along their interspaces—plane pol × 75.

Fig. 12—Celestite (black occupying the fractures across the phosphatic material (white)—negative print.

of gastropods, forums and ostracods. Presence of glauconite pellet is another conspicuous feature.

Of the two igneous apatite deposits in India, the Singbhum apatite is intimately associated with magnetite and is highly fractured, indicating that the probable formation took place during shearing movements. The occurrence of magnetite along the fractures within the deformed apatite grains indicates that the magnetite has been introduced later. This is also suggested by the commonly noted interstitial nature of the magnetite in relation to apatite. Magnetite also occurs as disseminated megascopic crystals. In some places, as in Ramchandrapahar area, apatite occurs without magnetite. These features and also the absence of severe deformation of the magnetite indicate that the crystallization of the two minerals was separated in time. The apatite has been identified as relatively pure fluoroapatite with $N_o = 1.632 \pm .002$ and $N_e = 1.627 \pm .002$.

In the Kasipatnam area, Visakhapatnam district, apatite occurs as singled out fluoroapatite crystals sometimes as big as 2 ft. in length (Fig. 13) with $N_o = 1.642 \pm .002$ and $N_e = 1.638 \pm .002$. In some cases it occurs in association with magnetite and brown biotite and allanite but quite frequently they are mutually exclusive of each other.

Infrared Studies

The IR Spectra of ten typical samples as recorded in the 550—1800 cm^{-1} region are reproduced in Fig. 14 and the frequencies along with their classification of their $(PO_4)^{3-}$ and $(CO_3)^{2-}$ ions are tabulated in Table 1.

Fig. 13—Perfectly developed big hexagonal crystals of apatite.

TABLE 1—ASSIGNMENT OF IR BANDS FOR THE $(CO_3)^{2-}$ ION OF THE SAMPLES

Samples	ν_1	ν_2	ν_3	ν_4
Free $(CO_3)^{2-}$ Ion	..	879	1415	680
Calcite	..	874	1430	710
Aragonite	1080	866	1492	711, 506
Simple ionic carbonates	1090-1020	890-820	1504 1470-1420	750-680
Carbonatoapatite (Synthetic)	..	872	1462 1411	..
Francolite	..	865 874	1452 1428	..
Kanpur	..	878	1455 1430	..
Maton	..	862	1455 1430	..
Jaisalmer	..	872	1452 1425	710
Paritibba	..	862	1455 1425	..
Kimoi	..	872	1455 1425	..
Masrana	..	870	1452 1425	..
Nainital	..	863	1454 1425	
Tiruchirapalli	..	868	1455 1425	710
Singbhum	..	..	..	..
Kasipatnam	..	870	1455 1420	..

ASSIGNMENT OF IR BANDS FOR THE $(PO_4)^{3-}$ ION OF THE SAMPLES

Samples	ν_1	ν_2	ν_3	ν_4
*Free $(PO_4)^{3-}$	x	x	1080	600
*Hydroxyapatite (Synthetic)	959	x	1090 1025	628, 602, 563
*Fluorapatite (Synthetic)	964	x	1090 1036	740, 602, 575
*Carbonatoapatite (Synthetic)	959	x	1090 1026	602, 563
Kanpur	960	x	1094 1045	600, 568
Maton	960	x	1093 1043	600, 570
Jaisalmer	960	x	1090 1040	600, 565
Paritibba	963	x	1093 1040	601, 570
Kimoi	965	x	1095 1040	600, 565
Masrana	962	x	1092 1040	600, 565
Nainital	963	x	1092 1040	601, 570
Tiruchirapalli	965	x	1090 1040	640, 600, 575
Singhbhum	962	x	1090 1040	742, 601, 575
Kasipatnam	962	x	1090 1040	740, 601, 565

*Reference-7.

These studies show that the Singbhum variety is relatively pure fluoroapatite with a medium weak intensity band at 742 cm^{-1}. The presence of this band in an apatite was interpreted as a characteristic feature of pure fluoroapatite as discussed in an earlier communication[9]. Kasipatnam variety has also shown a broadened absorption at the same position, and also presence of a little carbonate substitution. It has been interpreted as partially substituted fluoroapatite matrix. All the other varieties excepting the above two, have been identified as carbonato-fluoroapatites, with varying degrees of CO_3 substitution. Jaisalmer and Tiruchirapalli have maximum carbonate content and Kimoi and Masrana have least substitution. Jaisalmer and Tiruchirapalli have also given sharp peaks at 710 cm^{-1}, which indicates the presence of calcite as one of the descrete phases.

Most of the samples contain quartz, which is characterised by the appearance of the bands at 695,795 and 775 cm^{-1}. One variety of apatite, namely, Tiruchirapalli contains sulphate which is indicated by the presence of

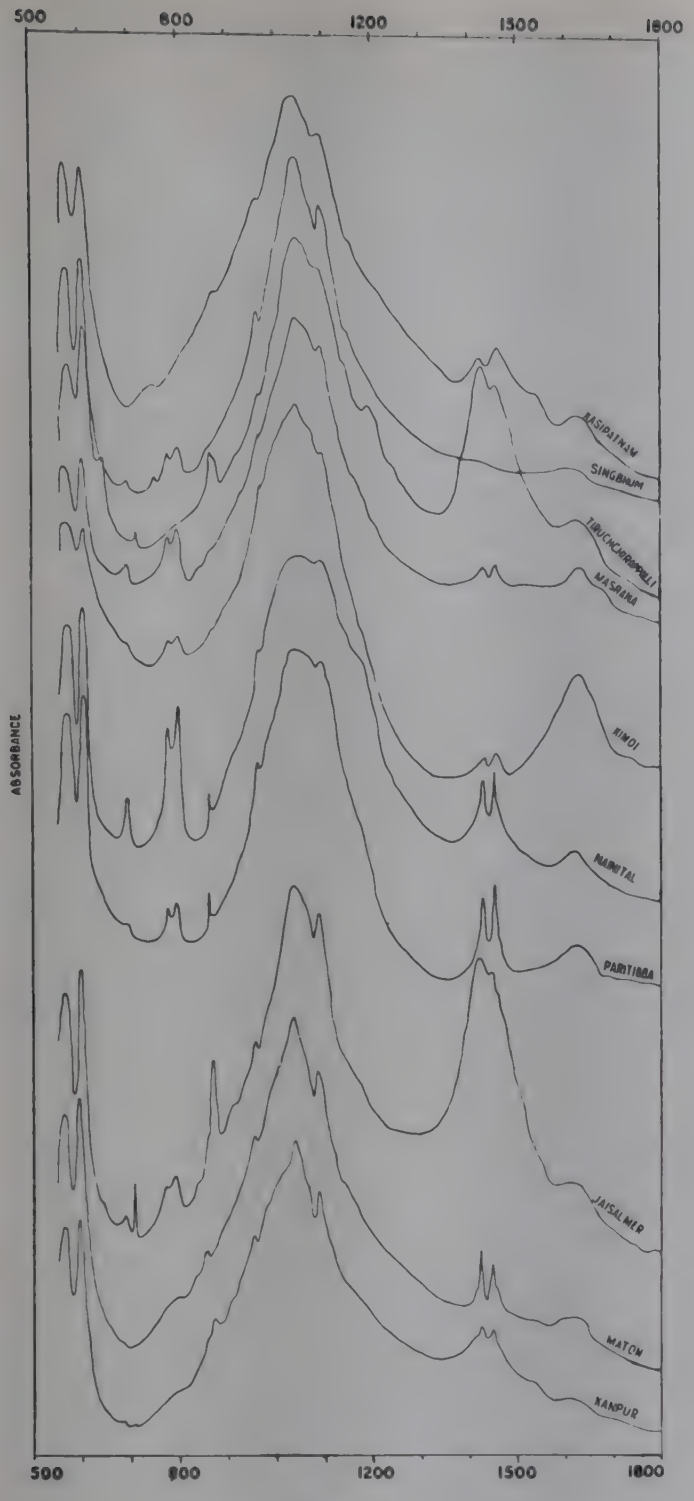

Fig. 14

a band at 1190 cm^{-1}. In most of the cases a hump at 1625 cm^{-1} is noticed which could be due to presence of hydroxyapatite or due to moisture absorption during KBr pellet preparation. In particular, however, Tiruchirapalli variety showed a band at 640 cm^{-1}, which has been interpreted as a definite presence of hydroxyapatite (c.f. collophane).

X-Ray Study

X-ray diffraction data are presented in Table 2 for ten typical samples. These studies reveal that francolite is the major constituent of all the rocks except the Singbhum variety. The major constituent in the Singbhum variety is fluoroapatite.

Free calcite has been detected in four cases, viz., Jaisalmer, Kanpur, Maton and Tiruchirapalli varieties. In other cases it may be present in the matrix, probably, less than 3 per cent, or exist as tiny crystallites of particle size smaller than 100 A, linear dimension, and escape detection by X-rays. Quartz has been detected in all the samples except Kasipatnam. In Tiruchirapalli variety strontium sulphate is also present.

Discussions

The microscopic, infra-red and x-ray investigations, in general, corroborate each other's findings and indicate that Singbhum variety is dominantly fluoroapatite while the rest are all substituted products thereof with introduction of carbonate and hydroxy groups. In the case of Kasipatnam variety, this introduction is perhaps limited to a lower degree but the optical data favour substitution of fluorine by chlorine somewhere around the 75:25 ratio[8]. It should be mentioned however that the composition of apatites varies in so many ways that any accurate correlation of optic data with differential substitution always remains questionable. It may be noted that collophane, so commonly identified by microscopic study of many of the samples due to their low birefringence, being cryptocrystalline, has been missed in the X-ray investigations.

Mining and Economic Feasibilities

Though the actual reserves of the phosphate deposits belonging to the Kanpur-Maton area have not yet been determined, it is presumed that these will prove to be one of the biggest of all the hitherto discovered rock phosphate deposits in India. The P_2O_5 content assay, on an average, between 15 - 25 per cent falls short for the requirement for manufacture of superphosphate. Moreover intimate association of these with calcareous material has rendered the quality of the phosphatic rock still poorer. In case of Jaisalmer phosphate, association of high $CaCO_3$ has been observed. The P_2O_5 content is around 15 - 20 per cent and the total reserve estimated will be of the order of 4.8 million tons. Thus it will be quite apparent that beneficiation of these phosphatic materials will be an essential prerequisite. CO_2 content of all these deposits is, in most cases, higher than 10 per cent.

TABLE 2—X-RAY DATA FOR INDIAN ROCK-PHOSPHATE

Kanpur 1		Maton 2		Jaisalmer 3		Paritibba 4		Kimoi 5		Masrana 6		Nainital 7		Tiruchirapalli 8	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
				4.30	vw	4.30	vw			4.30	vw	4.28	ms		
4.10	vvw	4.10	vvw											4.08	vvw
3.90	vvw	3.90	vvw	3.90	vvw	3.90	vvw							3.90	vvw
3.45	w	3.45	w	3.48	w	3.48	w	3.48	w	3.48	w	3.45	w	3.48	w
3.35	m	3.35	m	3.38	m	3.38	m	3.38	m	3.35	m	3.36	m	3.35	m
3.18	vw	3.18	vw	3.18	vvw	3.20	vw	3.20	vw	3.20	vw	3.20	vw	3.19	vw
3.08	w	3.08	w	3.08	w	3.08	w	3.08	w	3.08	w	3.08	w		
3.05	m	3.05	m	3.05	m									3.05	m
2.90	vvw	2.90	vvw			2.90	vvw							2.98	m
2.80	s	2.80	s	2.80	s	2.80	s	2.80	s	2.80	s	2.80	s	2.80	s
2.78	w	2.78	w	2.78	w	2.78	w	2.78	w	2.78	w	2.78	w	2.78	w
2.70	s	2.70	s	2.70	s	2.70	s	2.70	s	2.70	s	2.70	s	2.70	s
2.63	w	2.63	w	2.63	w	2.63	w			2.62	w	2.62	w	2.63	w
				2.52	vvw	2.55	vvw			2.55	vvw	2.57	vvw		
				2.50	vvw	2.47	vvw	2.47	vvw	2.46	vvw	2.46	vvw		
						2.41	w					2.38	vvw		
2.30	vvw	2.30	vvw	2.29	vvw	2.29	vvw			2.28	vvw	2.28	vvw	2.29	vvw
2.25	w	2.25	w	2.25	w	2.25	w	2.25	w	2.25	w	2.26	w	2.25	w
				2.15	vvw			2.18	vvw	2.14	vvw	2.14	vvw		
				2.10	vw										
				2.07	vvw	2.07	vvw	2.07	vvw	2.00	vvw			2.05	vvw
				2.00	vvw	2.02	vvw	2.02	vvw			1.98	vvw	2.01	vvw
1.93	vw	1.93	vw	1.93	vw	1.93	vw	1.93	vw	1.93	vw	1.93	vw	1.93	vw
				1.89	vvw	1.89	vvw	1.89	vvw	1.88	vvw	1.88	vw	1.88	vw
1.84	vw	1.84	vw	1.84	vw	1.84	vw	1.84	vw	1.84	vw	1.84	vw	1.84	vw
1.795	vvw	1.795	vvw	1.795	vvw	1.795	vvw	1.795	vvw	1.795	vvw	1.795	vvw	1.795	vvw
1.770	vw	1.770	vw	1.770	vw	1.770	vw	1.770	vw	1.770	vw	1.770	vw	1.770	vw
1.745	vvw	1.745	vvw	1.745	vvw	1.745	vvw	1.745	vvw	1.745	vvw	1.745	vvw	1.745	vvw
1.720	vvw	1.720	vvw	1.720	vvw	1.720	vvw	1.720	vvw	1.720	vvw	1.720	vvw	1.720	vvw
				1.640	vvw	1.640	vvw	1.640	vvw	1.640	vvw	1.640	vvw	1.640	vvw
				1.620	vvw	1.620	vvw	1.620	vvw			1.620	vvw	1.630	vvw
						1.550	vvw	1.550	vvw	1.540	vvw	1.540	vvw		
				1.47	vvw	1.47	vvw								

Lattice dimensions:
For samples from Kanpur to Kasipatnam

a=9.34Å
c=6.89Å

*D. McConnell, *Bull. Soc. Fr. Mineral Cristallogr.*, 75, (1952), 428 **A.S.T.M. Data Card.

So far as the Uttar Pradesh group of phosphates are concerned, particularly the deposits of the Mussoorie synform, the approximate total reserve may be tentatively put around 35 million tons. The P_2O_5 content assay is 15 per cent on average. Here the calcareous materials are low and the gangue consist chiefly of argillaceous and siliceous material. However it should be noted that these inferences have been drawn from a study of the samples collected from shallow pits and trenches within the phosphoria formation which is considerably weathered. It is therefore very likely that due to leaching the P_2O_5 content in the formation might have been enriched and $CaCO_3$ content decreased. Another factor needs due consideration for these deposits; that these are mostly located at an altitude of 6500 feet, on an average, and are distributed within a 120 Km zone of difficult terrain. As such the transportation feasibility of mined material to the nearest railway head, possibly by ropeway, should be viewed in the perspective of the correct reserves, their location, sectors and blocks etc.

The Nainital phosphate horizon appear to be of local nature and needs further investigation.

The phosphatic nodules of Tiruchirapalli region do not offer feasibilities for economic exploitation because of their extremely sporadic distribution.

In Singbhum region, small-scale mining of apatite has been taken up for a pretty long time but the production, which was too meagre to meet the demands for fertilizer manufacture, was utilised by Indian Iron and Steel Company. However, it has been reported that on the basis of the discovery of a rich deposit occurring in twelve places along the Singbhum shearzone, a

TABLE 2—X-RAY DATA FOR INDIAN ROCK-PHOSPHATE (*Contd.*)

Kasipatnam 9		Singbhum 10		Francolite* 11		Fluoroapatite** 12		Hydroxyapatite 13		hkl† 14		Calcite 15		Quartz 16		$SrSO_4$ 17	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
		4.28	w														
														4.25	25		
4.10	vvw	4.08	vvw	4.04	25					200							
3.90	vvw	3.89	vvw	3.86	15					111							
3.45	w	3.45	vw	3.44	25	3.44	20	3.44	40	002						3.42	14
		3.35	m											3.35	100		
3.19	vw	3.18	w	3.16	15			3.11	8	102						3.16	21
3.08	w	3.08	w	3.06	50	3.07	30	3.08	30	120							
												3.40	100				
																2.97	100
2.80	s	2.80	s	2.79	90	2.80	100	2.81	100	121		2.845	3				
2.78	w	2.78	ms	2.77	35	2.78	40	2.78	60	112							
2.70	s	2.71	ms	2.70	100	2.71	60	2.72	60	300						2.70	72
2.63	w	2.62	m	2.62	20	2.63	30	2.62	8	202							
2.52	vvw	2.52	vvw	2.51	10	2.53	5			301							
		2.46	vvw			2.49	5					2.495	14	2.45	15		
2.82	vvw	2.28	vvw	2.29	10	2.30	5	2.27	16	122		2.285	18	2.29	10		
2.26	w	2.25	w	2.25	65	2.26	20			130				2.23	6	2.26	14
		2.15	vvw	2.13	10	2.14	10	2.13	4	131							
		2.12	vw											2.12	9		
2.06	vvw	2.06	vvw	2.06	10	2.06	10	2.06	4	113		2.095	18			2.03	43
		1.98	vvw			2.00	5			203				1.97	8		
1.94	vw	1.94	m	1.934	20	1.94	40	1.94	20	222		1.297	5			1.94	14
1.87	vvw	1.88	vvw	1.883	15	1.89	10			132		1.875	17			1.88	14
1.84	vw	1.84	ms	1.836	20	1.84	60	1.84	20	123				1.82	25	1.84	14
1.795	vvw	1.800	w	1.792	20	1.80	30			231							
1.770	vw	1.770	vvw	1.770	40	1.77	30			140							
1.750	vvw	1.750	w	1.745	15	1.75	30			402							
1.720	vvw	1.720	w	1.720	10	1.72	30	1.71	16	004							
		1.640	vvw			1.64	10			232, 322				1.66	8		
						1.61	5			133, 313		1.626	4				
		1.540	vvw			1.54	5			240, 420		1.525	5	1.54	20		
		1.47	w			1.47	20	1.45	8	502		1.473	2	1.45	2		
		a=9.38Å		a=9.34Å		a=9.38Å		a=9.42Å									
		c=6.88Å		c=6.89Å		c=6.88Å		c=6.88Å									

†Orthohexagonal indices.

beneficiation plant is being set up at Adityapur near Jamshedpur. This plant is expected to supply the requirement of about 45,000 tons of rock phosphate per year to the superphosphate factory at Sindri.

In Kasipatnam area several veins of apatites are now being mined simultaneously. The P_2O_5 content of these apatite is as high as 40 per cent. on an average, but the reserve is not sufficiently encouraging to meet the demands of a fertilizer industry. The estimated reserves of the area will be around 80,000 tons.

Acknowledgements

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Determination of Retention Indices of Saturated Hydrocarbons by Graphical Methods*

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Several methods of determining Kovats' retention indices of saturated hydrocarbons have been discussed. A linear relationship has been observed in retention indices of alkyl and cyclic paraffins between two stationary liquids belonging to non-polar or moderately polar groups. Retention index of a compound available in one stationary liquid can be determined in a second solvent. When separate straight lines are drawn for properly chosen homologous series and family members, the data can be read accurately within ± 1 index unit. The criteria for the classification into homologous series and family members and also for the selection of a suitable pair of stationary liquids have been dealt with mathematically. By these methods retention indices of 43 alkyl and 48 cycloparaffins have been computed in SE-30.

Approximate methods of finding retention indices in a stationary liquid have been based on separate linear plots of logarithm of retention indices of family and homologous members of all saturated hydrocarbons against their reciprocal boiling points. Retention indices of hydrocarbons at two temperatures in a stationary liquid have been found to give linear plots.

The principle of additivity based on empirical rules which do not consider detailed structural features of solute molecules are considered unsuitable for prediction of retention indices. However, retention indices of most hydrocarbons in a non-polar stationary liquid can be evaluated with a fair degree of accuracy from vapour pressures at the column temperature. Certain generalisations have been observed in the order of elution of different types of hydrocarbons.

It is well known that gas chromatography (GC) is lagging in its identifying ability compared to its separation power which is unparalleled by any other technique. The main reason is the poor reproducibility of the identification parameters like relative and specific retention data. In order to cancel out the disturbing effects Kovats [1,2] proposed a retention index system based on the use of two adjacent normal paraffins (between which a solute elutes) as standards. Increasing number of articles [3–7] in recent journals on various aspects of retention index bears testimony to the usefulness of this system. The present authors[8] have developed a new parameter based on the temperature coefficient of retention index of a solute for its sure identification.

A great limitation to the large scale use of retention index is that the values of all the compounds dealt with are either to be determined experimentally with pure standards or to be collected from literature for a given column at the desired temperature. The present study aims at finding out retention indices in a stationary liquid from the corresponding data available in a second solvent and also for inter-conversion of retention indices of solutes in a given partitioning liquid at any two temperatures.

Theory

Two methods have been used in this study for the graphical determination of retention index. The first method is based on the observation that the indices of a carefully chosen group of compounds from hydrocarbons and other compound types in two suitable stationary liquids bear a linear relationship. The two stationary liquids should preferably be of similar

*This is a part of the paper presented at the Gas Chromatography Symposium of the 55th Indian Science Congress Session at the Banaras Hindu University during 3-10th January, 1968.

polarity or in other words, the nature of retentive forces exerted by the two stationary liquids on these so-called 'family' of compounds should be similar. A guideline for the selection of homologues and family members and a proper pair of stationary liquids can be obtained from activity coefficients.

Incorporating into the definition of retention index proposed by Kovats[2] the thermodynamic relation of retention volume of a solute with its vapour pressure and activity coefficient one gets the following equation

$$CI' = \log \frac{P^\circ_n}{P^\circ_x} + \log \frac{\gamma_n}{\gamma_x} \qquad (1)$$

where,

$C = \log \frac{V'_{n+1}}{V'_n}$ = Constant for a given stationary liquid.

V' = adjusted retention volume corrected to gas hold-up

Subscript n = carbon number of the lower normal paraffin.

Subscript x = stands for solute.

p° = vapour pressure.

γ = activity Coefficient.

$$I' = \frac{I - 100\ n}{100}$$

When a solute elutes at a given temperature between the same pair of normal paraffins in two stationary liquids denoted by subscripts 1 and 2 the following equation can be derived:

$$I'_1 = \frac{C_2}{C_1} I'_2 + \frac{1}{C_1} \log \frac{(\gamma_x/\gamma_n)_2}{(\gamma_x/\gamma_n)_1} \qquad (2)$$

It has been assumed that the term P_n°/P_x° is not affected significantly by two stationary liquids of comparable polarity, especially when the solid support is the same in both cases. The plot of I_1' against I_2' (hence of retention indices in one liquid against another) for a group of solutes will be linear only when the last term of equation (2) is constant. In other words, those solutes whose activity coefficients relative to the corresponding normal paraffins bear constant ratios in two stationary liquids will form a close knit homologous series and give linear plot of their retention indices. It is not essential for the column temperature to be identical in both stationary liquids to give linear plots. It follows from eqution (1) that for the same or two stationary liquids at two column temperatures t_1 and t_2.

$$I'_t = \frac{C_{t_2}}{C_{t_1}} I'_{t_2} + \frac{K}{C_{t_1}} \log \left(\frac{\gamma_x/\gamma_n}{\gamma_x/\gamma_n}\right)^{t_2}_{t_1} \qquad (3)$$

where, constant $K = \log \left(\frac{P_n^\circ}{P_x^\circ}\right)_{t_1} - \log \left(\frac{P_n^\circ}{P^\circ_x}\right)_{t_2}$

When the last term of equation (3) is constant I_{t_1} against I_{t_2} will give a linerar plot. It is a convention [9] to use δ to denote the difference of retention index of two solutes in the same stationary liquid and Δ for the same difference in two stationary liquids.

The second method is based on the linearity of logarithm of retention index against reciprocal of boiling points of a properly chosen group of homologous hydrocarbons and their family members. This is, however, an approximate method.

Experimental*

Chromosorb W, 60/80 mesh, acid washed and silanized was coated with approximately 5 per cent silicone rubber gum SE-30** by the percolation technique. A 1/8″ O.D. copper refrigeration tubing thoroughly cleaned and dried was packed in 10′ sections in the shape of U-tubes by gentle tapping with a rubber-padded glass rod. Sections were connected by swagelok unions. Columns of 20′ or 30′ were used in this investigation with nitrogen as carrier gas. The gas chromatograph was Aerograph Hi-Fi model 600D fitted with a flame ionization detector. The gas hold-up was determined from methane retention time which was found in good agreement with the direct air-peak method of Hilmi[10]. The control of column variables like temperature and pressure was fairly good.

Results

Alkanes

Linearity of I in two Stationary Liquids: Retention indices of isoparaffins in hexadecane were plotted against the corresponding values in squalane[11], the column temperature being 25°C in both the stationary liquids, (line A in Fig. 1). A single straight line was drawn to fit all paraffins; the scatter in the data is within ± 2 index units. Better accuracy can be obtained by drawing separate straight lines to fit individual groups of homologues and family members. This was demonstrated in Fig. 2, where solutes were subdivided into mon-, di- and tri-substituted paraffins. Fig. 2 was utilized in determining I of various alkanes in SE-30 (Table 1) from all available (and reliable) data in squalane [11,12]. These

*Most of the reference hydrocarbons were purchased from the Phillips Petroleum Co. of U.S.A. and a few were received as gifts from the Associated Octel Co. Ltd., London.

**of General Electric, U.S.A.

indices are accurate within ± 1 unit. When I of a hydrocarbon was available in a non-polar stationary liquid other than squalane (SQ) the principle followed was to draw similar graphs as in figs. 1 and 2 between that stationary liquid and squalane or directly between that stationary liquid and SE- 30. The stationary liquids thus examined include hexadecane (HD)[13], hexatriacontane (HTK)[14], benzyl diphenyl (BDP)[14], high vacuum silicone grease (HVSG)[15], paraffin wax (PW)[16], hexadecane-fluolubrol mixed phase (HDFL)[17]. Retention indices in these stationary liquids were computed from retention data available in literature and hence included in Table 1. In all the cases linear plots of I in two stationary liquids were obtained. This principle can be extended to suitable pairs of stationary liquids of medium and strong polarity.

The linearity of retention indices of hydrocarbons in a given liquid at two temperatures was illustrated in Fig. 3. These plots can be utilized in determining indices at different temperatures in any stationary liquid.

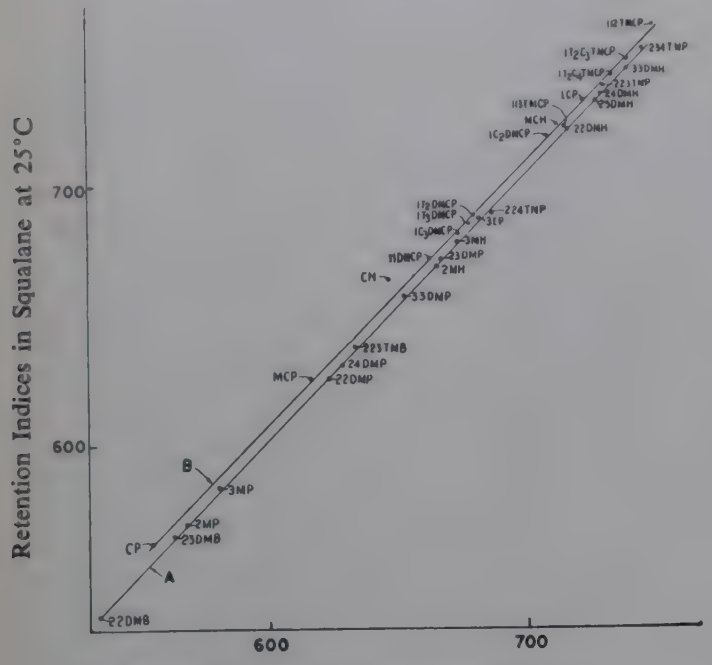

Fig. 1—Plot of Retention Indices in Two Non-Polar Liquids.
Line A—Alkyl Paraffins
Line B—Cyclic Paraffins

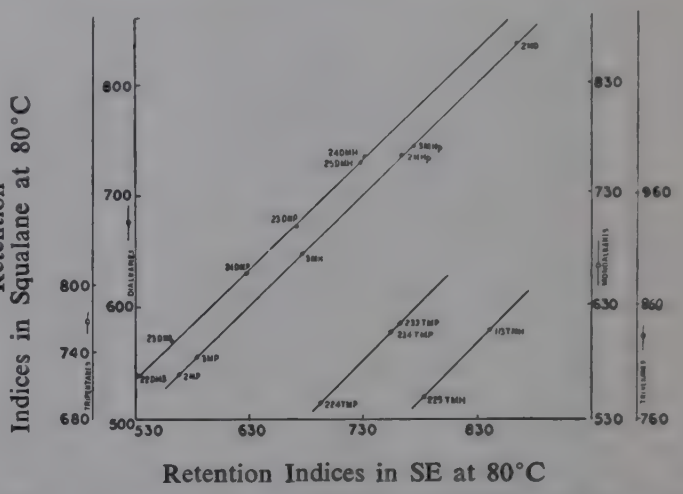

Fig. 2—Determination of Retention Indices of Mone, Di and Tri-Alkanes is SE-30.

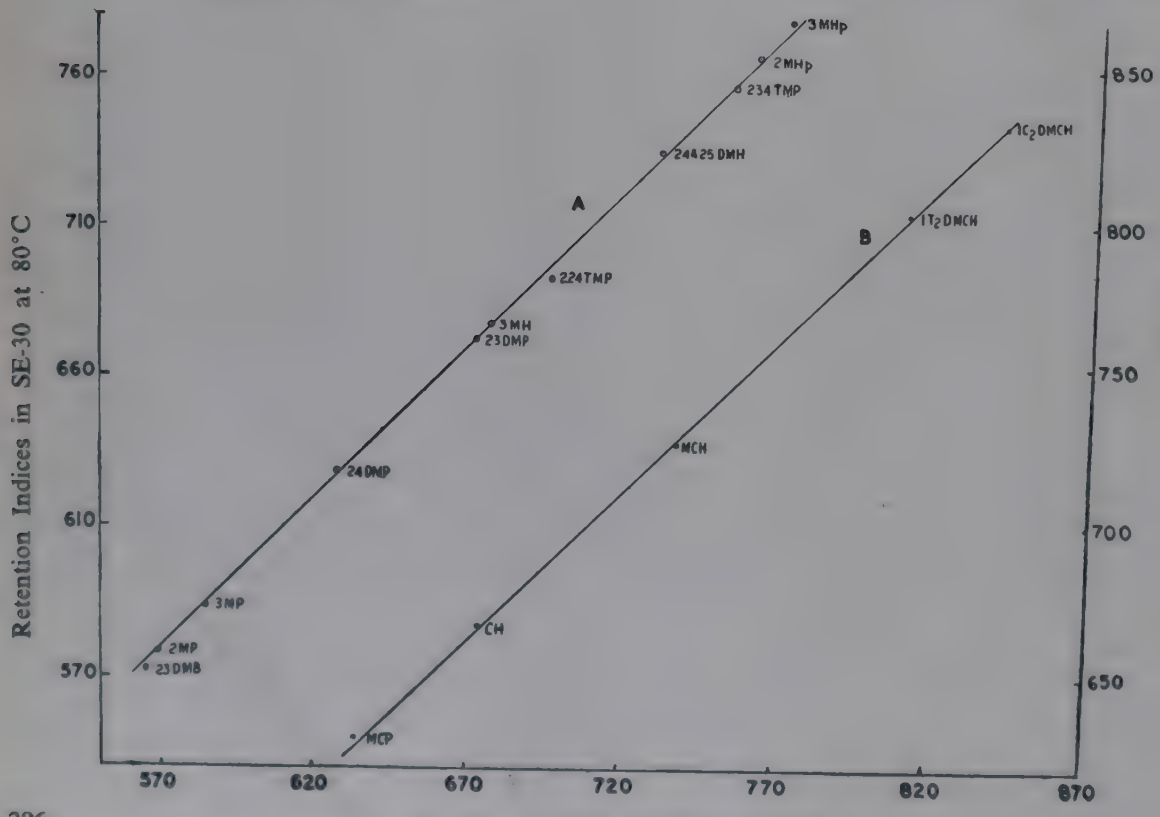

Fig. 3—Retention Indices of Alkanes (A) and Napthenes (B) in a Stationary Liquid between two Temperatures.

TABLE 1—RETENTION INDICES OF ALKYL PARAFFINS IN VARIOUS STATIONARY LIQUIDS

Compound[a]	SE-30 80°C	SQ. 80°C	SQ. 25°C	HD 25°C	HTK 78.5°C	BDP 78.5°C	HVSG 95°C	PW 78.5°C	HDFL 25°C
22 DMB	530[b]	539[d]	535	534	531	527	—	532	536
23 DMB	562[b]	569[d]	566	563	569	566	—	571	565
2 MP	568[b]	570[d]	570	568	569	568	571	569	573
3 MP	583[b]	585[d]	584	581	585	585	586	586	583
22 DMP	622	626	625	624	625	613	—	628	626
24 DMP	628[b]	630[d]	630	629	628	616	—	633	631
223 TMB	643	643	637	632	642	629	—	—	635
33 DMP	660	662	656	653	662	662	—	664	654
23 DMP	672[b]	672	670	667	674	668	—	675	668
2 MH	667	667	667	666	666	658	670	667	667
3 MH	677	677	676	674	677	671	679	678	674
3 EP	688	688	685	682	689	684	—	688	682
224 TMP	692[b]	694[d]	687	687	691	674	—	691	690
2233 TMB	—	733	720	—	—	—	—	—	—
22 DMH	721	722	718	716	715	705	725	722	719
25 DMH	728[b]	729	728	727	725	714	733	729	731
24 DMH	731[b]	734	731	729	730	720	—	734	733
223 TMP	739	742	734	730	740	733	—	741	733
33 DMH	746	747	740	739	745	737	—	747	743
234 TMP	754[b]	758	748	745	755	751	—	757	750
233 TMP	762	765	755	—	765	760	—	763	755
23 DMH	761	761	758	—	760	757	—	761	761
2 M3EP	763	764	759	—	763	762	—	773	760
2 MHp	764[b]	765[d]	764	—	762	758	767	764	770
4 MHp	769	768	767	—	766	762	—	769	771
34 DMH	773	774	768	—	773	773	—	774	770
3 M3Ep	781	780	769	—	770	788	—	779	770
3 EH	776	775	771	—	772	773	—	782	774
3 MHp	775[b]	773	770	—	771	758	776	—	775
2244 TMP	—	—	768	—	—	—	—	—	—
225 TMH	783[b]	778	—	—	—	—	—	—	—
224 TMH	794	—	—	—	—	—	—	—	—
235 TMH	818	—	810	—	—	—	—	—	—
22 DMHp	820	—	808	—	—	—	822	—	—
24 DMHp	823	822[e]	—	—	—	—	—	—	—
26 DMHp	828	827[e]	—	—	—	—	831	—	—
25 DMHp	834	833[e]	—	—	—	—	—	—	—
113 TMH	842	—	834	—	—	—	—	—	—
23 DMHp	858	856[e]	—	—	—	—	—	—	—
2 MO	865[b]	864[e]	—	—	—	—	865	—	—
3 MO	871	870	—	—	—	—	872	—	—
4 MO	860	859[e]	—	—	—	—	—	—	—
4 MN	961[b]	—	—	—	—	—	—	—	—

a=see reference (9) for abbreviation; D stands for di; T for tri and tetra as the case may be, M for methyl, B for butane, P for pentane, H for hexane, Hp for heptane, O for octane, N for nonane, and E for ethyl.

b=values determined by injecting pure compounds.

d=values checked experimentally,

e=values computed from reference (21).

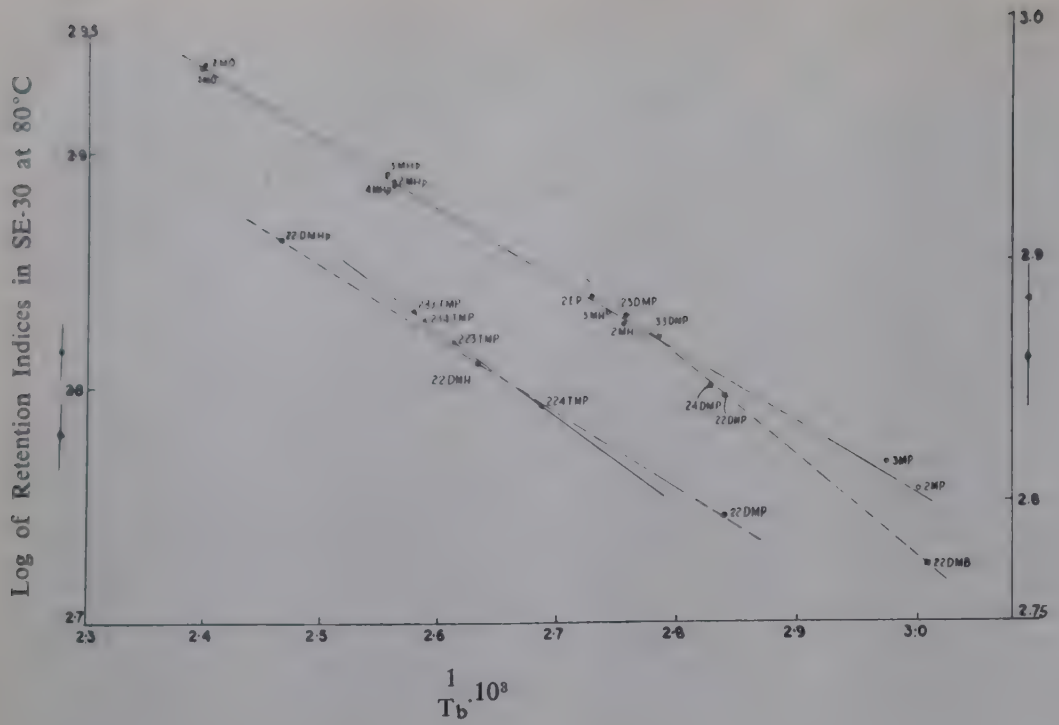

Fig. 4—Relation of Retention Indices with Boiling Points of Alkyl Paraffins.

When alkanes are subdivided into homologous groups and family members logarithms of their retention indices have been found to give linear relation with reduced boiling points in non-polar stationary liquids. A few illustrations were given in Fig. 4. It is noted that the randomness of data in Fig. 4 is somewhat more than those in Fig. 2. However, the retention indices of homologues and family members can be determined approximately from boiling points.

Cyclopentanes

It was established in Fig. 5 that the retention indices of cyclopentanes in SE- 30 and in other non-polar stationary liquids, namely, hexadecane, squalane and hexatriacontane give linear plots. Hence, I of a cyclopentane available in these stationary liquids was converted to the corresponding value in SE- 30 at 130°C with the help of Fig. 5. When the values of I in SE- 30 were derived from more than one non-polar liquids an average was taken. These data were given in Table 2; the values are accurate within ± 2 index units. It can be noted from Fig. 5 that retention index of a cyclopentane in non-polar stationary liquids decreases in the order of hexatriacontane > squalane > hexadecane, indicating a probable use of this phenomenon in the classification of stationary liquids.

It was shown in Fig. 6 that logarithm of I against reciprocal of boiling points (T_b). bears linear relationships for mono- (line A), di-(line B) and tri-alkyl substituted (line C) cyclopentanes in SE- 30 (or other non-polar stationary liquids). An approximate value of I can be obtained from such plots.

Cyclohexanes

Antheaume and Guiochon[18] have determined I of 34 cyclohexanes in SE-30 at 130°C. These values were found to be in agreement within ± 1 index unit when checked in our laboratory with a few pure cyclohexanes. It was shown in Fig. 3, (line B), that I of cyclohexanes

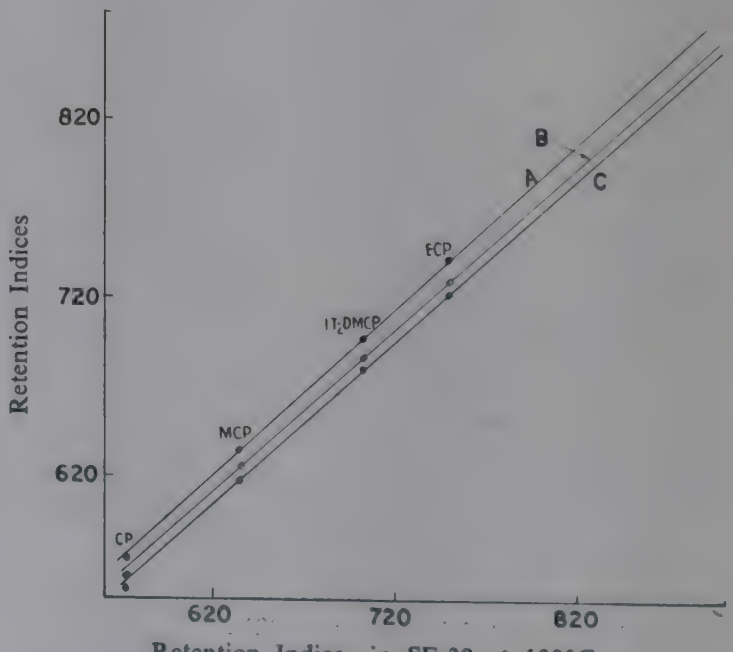

Fig. 5—Determination of Retention Indices of Cyclopentanes in SE-30. HTK at 78.5°C (A), Squalane at 25°C (B) and Hexadecane at 25°C (C).

TABLE 2—RETENTION INDICES OF CYCLOPENTANES IN NON-POLAR STATIONARY LIQUIDS

Compound[a]	SE-30 130°C	SQ. 25°C	HD 25°C	HTK 78.5°C	HDFL 25°C	SQ. 70°C
CP	572[b]	563	555	573	551	570[d]
MCP	634[b]	625	617	634	617	631[d]
11 DMCP	683	670	663	679	661	677[d]
1 C_3DMCP	694	679	674	689	672	686
1 T_3DMCP	698	683	678	—	676	690
1 T_2DMCP	702[b]	686	680	696	678	—
1 C_2DMCP	734	716	708	727	705	725
ECP	749[b]	729	722	741	721	738
113 TMCP	740	719	715	769[f]	716	—
1 T_3C_4 TMCP	759	738	733	—	736	—
1 T_2C_3 TMCP	766	744	738	—	742	—
112 TMCP	779	757	749	—	753	—
1 C_3T_4 TMCP	791	768	—	—	765	—
1 C_2T_3 TMCP	798	773	—	—	767	—
1 MT_3 ECP	810	785	—	—	783	—
1 MT_2 ECP	811	786	—	—	783	—
1 M1 ECP	814	788	—	801	783	—
1 C_2C_3 TMCP	821	794	—	—	789	—
1 MC_3 ECP	808	783	—	—	781	—
iso PCP	835	806	—	823	798	—
n PCP	851	—	—	838	819	834
1 C_2C_4 TMCP	797	—	—	—	770	—
1 MC_2 ECP	846	—	—	—	807	—

a, see foot note of table 1. C stands for cyclo, $1C_2$ and $1T_2$ stand for 1-cis-2 and 1-trans-2 respectively and so on.
f, value appears to be high.

at 80°C and at 130°C give a straight line plot which can be utilized in obtaining values at 80°C. I of cyclohexanes in SE-30 at 130°C from reference and of experimental data at 80°C were given in Table 3. Regarding 1-*cis*-3 and 1-*trans*-3 dimethyl cyclohexanes the indices reported by Antheaume and Guiochon should be reversed as shown in Table 4, because, all other *cis* and *trans* isomers follow the same order in their retention indices in both squalane and SE-30; also the higher boiling isomers have been observed to give larger I-values in non-polar stationary liquids. On comparison of the order of boiling points and retention indices of n-propyl and iso-propyl cyclopentanes and cyclohexanes in SE-30 and other non-polar phases the retention indices of n-butyl and iso-butyl cyclohexanes reported in reference (18) seem to have been interchanged and hence were

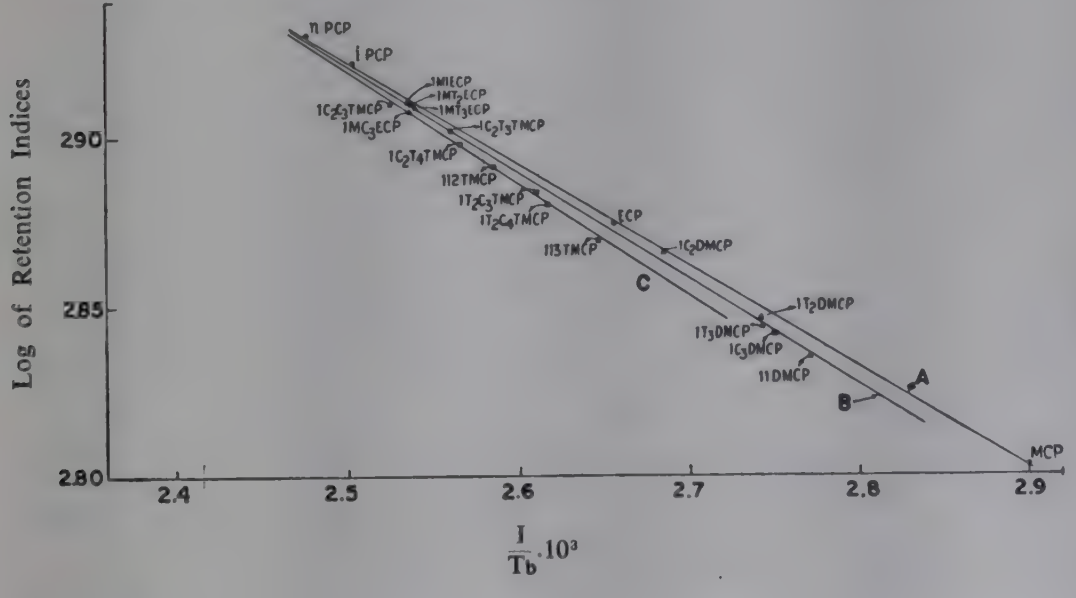

Fig. 6—Relation of Retention Indices with Boiling Points of Mono, Di, Tri-Alkyl Substituted Cyclopentanes in SE-30 at 130°C.

TABLE 3—RETENTION INDICES OF CYCLOHEXANES IN NON-POLAR STATIONARY LIQUIDS

Compound[a]	B.P. °C	SE-30 80°C	SE-30 130°C	SQ. 25°C	HTK 78.5°C	HDFL 25°C	SQ. 70°C
CH	80.7	667[b]	676[d]	662	672	645	668
MCH	100.9	727[b]	739[d]	720	735	711	730
1 T_4 DMCH	119.3	781	796	780	—	779	789
11 DMCH	119.5	784	—	780	796	776	792
1C_3 DMCH	120.1	783	798[f]	779	795	779	789
1T_3 DMCH	123.4	802[b]	817[d]	793	—	789	807
1C_4 DMCH	124.3	804	820	798	—	790	810
1T_3 DMCH	124.4	806	823[f]	799	—	790	810
1C_3 DMCH	129.7	831[b]	850[d]	—	—	811	836
ECH	131.8	825	842	828	845	818	839
135 TMCH (t)	138.0	—	840	—	—	—	—
135 TMCH (c)	140.0	—	870	—	—	—	—
123 TMCH (t)	143.0	—	954	—	—	—	—
123 TMCH (c)	145.0	—	982	—	—	—	—
124 TMCH (t)	145.0	—	868	—	—	—	—
124 TMCH (c)	146.0	—	895	—	—	—	—
iso PCH	154.5	—	934	—	—	—	923
n PCH	156.7	—	944	—	—	—	931
1 MT_4 iso PCH	161.0	—	997	—	—	—	—
1245 TMCH	164.0	—	1036	—	—	—	—
1 MC_4 iso PCH	168.5	—	1000	—	—	—	—
1245 TMCH	171.0	—	1054	—	—	—	—
iso BCH	171.0	—	1005[f]	—	—	—	983
14 DECH	174.0	—	1072	—	—	—	—
			1105				
13 DECH	175.0	—	1017	—	—	—	—
n BCH	180.9	—	1061[f]	—	—	—	1029

a, see foot notes of tables 1 and 2.

f, values corrected as shown in table 4.

TABLE 4—IDENTIFICATION OF 1T_3 AND 1C_3 DIMETHYL-CYCLOHEXANES AND BUTYL-CYCLOHEXANES

Compound	BP °C	Retention indices			
		SE-30[18] 130°C	SQ.[21] 70°C	SQ.[11] 25°C	Corrected* SE-30 130°C
1C_3 DMCH	120.1	823	789	779	798
1T_3 DMCH	124.4	798	810	799	823
iso BCH	171.0	1061	983	—	1005
n BCH	180.9	1005	1029	—	1061

*In a personal communication Professor G. Guiochon has agreed with our corrected values.

corrected in table 4. The linearity of retention indices of cyclohexanes in SE-30 and other non-polar liquids has been shown in Fig. 7.

Discussion

There are very few applications[19] of SE-30 at low temperatures. A good separation efficiency in SE-30 was observed by the present authors for hydrocarbons at low temperatures. Since SE-30 has a very wide temperature range from ambient to about 350°C it was considered worth while to determine and collect retention indices of all hydrocarbons in this stationary liquid. Retention indices in SE-30 and some other liquid phases were computed from retention data and chromatograms available in literature with the help of a semi-log paper[20].

(*a*) *General Rule of Elution Behaviour*: In SE-30 and also in other non-polar stationary liquids the elution of saturated hydrocarbons obey certain general rules. Cycloparaffins are retarded more compared to alkanes of equal carbon numbers. All mono and di-substituted paraffins elute between two adjacent normal paraffins of carbon numbers (n-1) and n; where n is the number of carbon atoms in the substituted alkane. Most tri-substituted alkanes elute between C_{n-1} and C_n; a few between C_{n-2} and C_{n-1} but the latter group has a tendency to elute in the former group at temperatures above 100°C. All tetrasubstituted alkanes elute between two normal alkanes C_{n-2} and C_{n-1}.

Unsubstituted and mono-substituted cycloparaffins elute between two adjacent normal paraffins C_n and C_{n+1}; di- and tri-substituted naphthenes elute in two groups, namely between C_n and C_{n+1}, C_{n-1} and C_n. In other words, higher the degree of branching greater is the lowering of retention indices of cycloparaffins of equal carbon atoms. This is true for isoparaffins also. This knowledge of the elution behaviour of all types of hydrocarbons will greatly help the interpretation of complex chromatograms.

(*b*) *Vapour Pressure and Structure:* Retention volumes or retention indices of non-polar solutes like the saturated hydrocarbons in non-polar stationary liquids are predominantly controlled by vapour pressures, activity

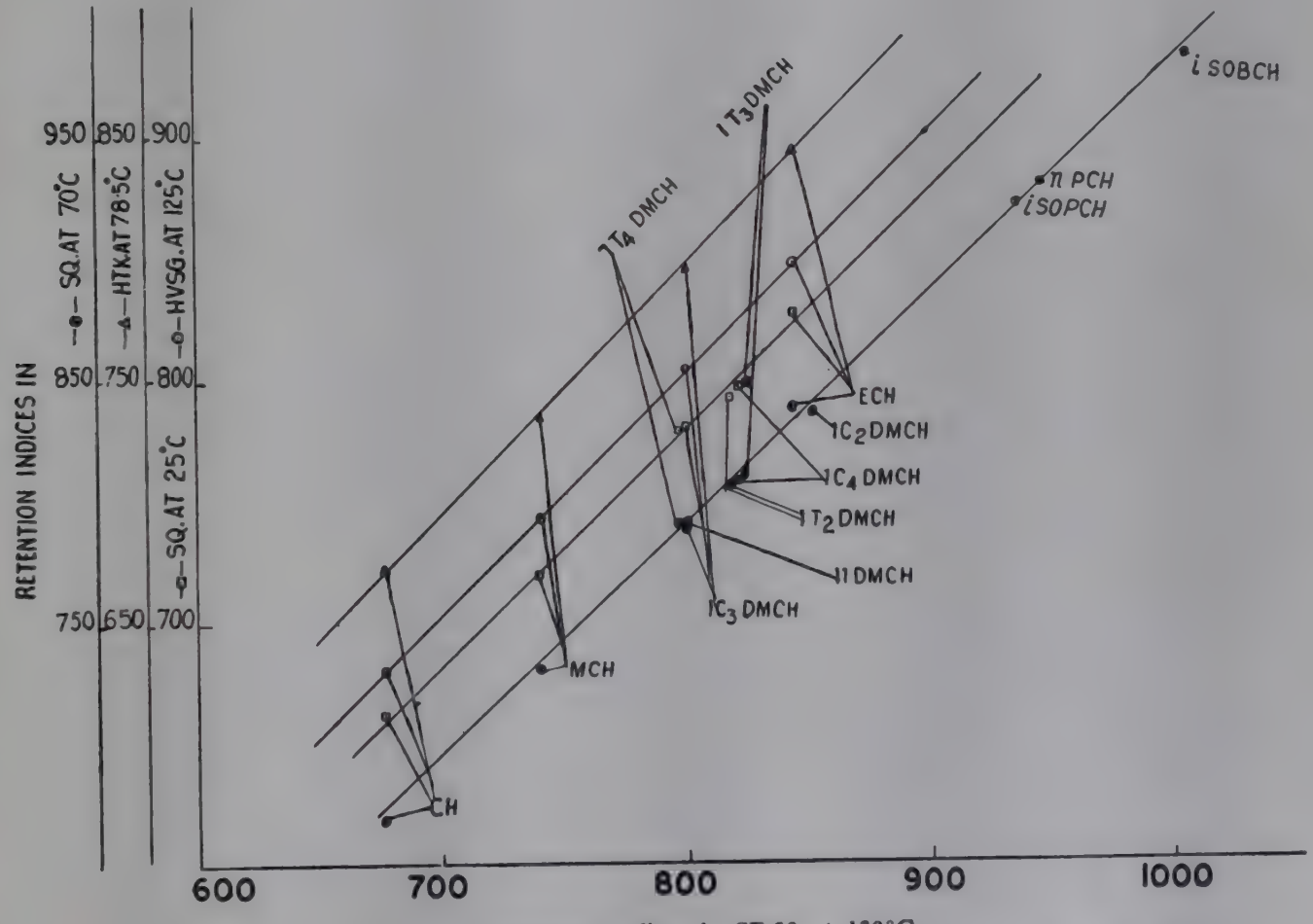

Fig. 7—Linearity of Retention Indices of Cyclophexanes in SE-30 and in other Non-polar Liquids.

coefficients playing a comparatively minor role. Perhaps, this had led to the common belief that all non-polar solutes in non-polar solvents are eluted strictly in the order of their vapour pressures. This is not true as is evident from the following observations (i) Table 5 where C_8 isomers (by way of illustration) with increasing retention indices do not show regular decrease in their vapour pressures and also from (ii) Table 6 containing pair of hydrocarbons of very close vapour pressures but of substantially different index values and vice versa.

TABLE 5—RETENTION INDICES AND VAPOUR PRESSURES OF C_8 HYDROCARBONS

Compound	ISE-30 80°C	V.P. (mm) 80°C
224 TMP	692	424
22 DMH	721	331
25 DMH	728	308
223 TMP	739	306
33 DMH	746	284
234 TMP	754	272
23 DMH	761	251
233 TMP	762	262
2 M3EP	763	252
2 MHp	764	232
4 MHp	769	230
34 DMH	773	234
3 MHp	775	222
3 EH	776	225
3 M3EP	781	236
$1T_3$ DMCH	802	203
$1C_2$ DMCH	831	164

TABLE 6—EFFECT OF STRUCTURE OF SATURATED HYDROCARBONS ON VAPOUR PRESSURE AND RETENTION INDEX

Compound	V.P. (mm) 80°C	ISE-30 80°C	Compound	ISE-30 80°C	V.P. (mm) 80°C
24 DMP	745	628	CP	560	1888
223 TMB	739	643	23 DMB	562	1448
CH	748	667	MCP	630	970
			24 DMP	628	748
2 MHp	232	764			
4 MHp	230	769	CH	667	745
34 DMH	234	773	2 MH	667	559
$1T_4$DMCH	230	781	MCH	727	394
$1C_3$ DMCH	222	783	25 DMH	728	308
3 MHp	222	775	$1T_4$DMCH	781	230
$1C_4$DMCH	200	781	3M3EP	781	236
$1T_3$ DMCH	203	802			

Activity coefficients of certain hydrocarbons may be significantly different although their vapour pressures are very similar. In other words, the structural features of hydrocarbons play an important role in the order of elution. Hence, assignment of peaks according to vapour pressure in a complex chromatogram even in a non-polar stationary liquid will be erroneous. A precise correlation of activity coefficient and of structure of solutes of known vapour pressures will no doubt result in a simpler method of predicting retention data.

(*c*) *Prediction of I from structure*: The prediction of retention index from the structure of solute molecules will be a great contribution in the identification capacity of GC and hence in making it the most ideal and self-sufficient single technique for analytical chemists. Schomburg[21] has made extensive studies in this regard with all types of hydrocarbons. However, Schomburg as well as Werhli and Kovats[1] in their empirical rules did not consider conformational and stereometric aspects of chemical structures. Their predicted values for even the simplest type of hydrocarbons, namely methyl paraffins are in error by 20 to 30 index units. The rule of additivity based on contributions of each methylene group in the main hydrocarbon chain and of each methyl group in the branched chain cannot give the desired accuracy in retention indices as can be noted from Table 7.

TABLE 7—CONTRIBUTION OF 2-METHYL GROUPS TOWARDS RETENTION INDEX

Method of calculation	I_2CH_3 in SE-30 at 80°C	Average
(a) Mono-Methyl series	68	
I_{2MP}–I_P	68	
I_{2MH}–I_H	67	66
I_{2MHp}–I_{Hp}	64	
I_{2MO}–I_{10}	65	
(b) Di-Methyl series		
I_{22DMP}–I_{2MP}	54	
I_{22DMH}–I_{2MH}	54	55
I_{22DMHp}–I_{2MHp}	56	
I_{23DMP}–I_{3MP}	89	
I_{23DMH}–I_{3MH}	84	85
I_{23DMHp}–I_{3MHp}	83	
(c) Trimethyl series		
I_{225TMH}–I_{25DMH}	55	
I_{224TMH}–I_{24DMH}	63	
I_{224TMP}–I_{24DMP}	64	70
I_{223TMP}–I_{23DMP}	67	
I_{233TMP}–I_{33DMP}	102	

The contribution of each methylene group in normal paraffins is 100 index units by definition. From the difference in the indices of two adjacent homologues the methylene contribution has been found to vary in SE-30 from 94 to 101 for monomethyl alkanes and from 89 to 110 for dimethyl paraffins. These fluctuations are not due to experimental errors and do not seem to follow any system upon which fairly accurate prediction can be made.

Methods of isolation of methyl group contribution in the 2-position (I_{2CH_3}) for mono-, di- and tri-methyl alkanes have been illustrated in Table 7. The randomness in the methyl contribution is rather small (exception 233 TMP) within any series than among the various series (This is true not only for SE-30 but also for all stationary liquids). The former effect shows some tendency to decrease with increase in the carbon number of the larger compound from which the methyl contribution is calculated. The second effect is due to mutual interaction of the substituents. The principles of additivity of constituent groups do not and cannot account for this highly complex interaction effect. This can only be explained by consideration of electronic configurations and detailed structural features of the hydrocarbon molecules along with the mode of interaction of the solute and solvent molecules.

Retention indices of all alkanes and naphthenes can, however, be evaluated from a simple linear relation of logarithm of vapour pressure against retention index, both at the same temperature. In Fig. 8 line A is for alkyl and line B for cyclic paraffins. Most of the values derived from Fig. 8 are likely to be accurate within $\pm$ 4 index units. This much of close approximation in the predicted I values will greatly simplify the interpretation of chromatograms of higher hydrocarbons. Those few compounds which are widely off the lines A and B will reveal a relatively strong dependence of activity coefficients on their retention data.

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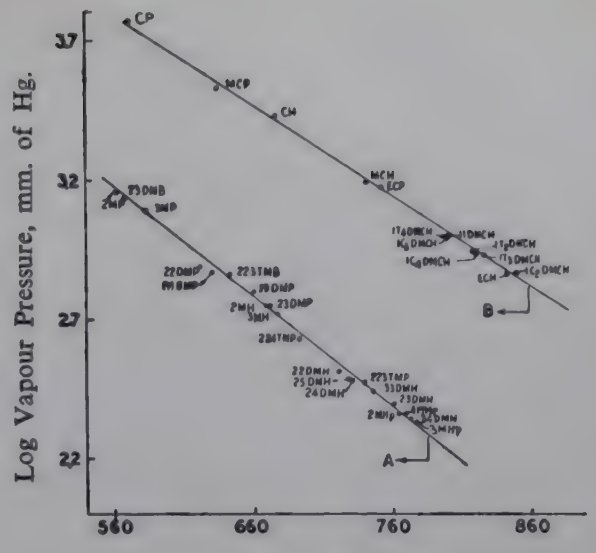

Retention of Indices.

Fig. 8—Relation of Retention Indices of Alkanes and Napthenes with Vapour Pressure.

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A Novel Subtraction Property of Silica Gel for Isoalkyl and Cyclic Paraffins

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Silica gel, modified by a combination of treatments with inorganic and organic compounds, has been found to retain irreversibly isoparaffins and cycloparaffins to the complete exlcusion of normal paraffins, olefins and aromatics. Studies on the mechanism of this unique subtraction property will lead to new methods of preparation of highly specific adsorbents for both analytical and industrial separations.

While working on the development of solid supports from silica gels for both gas-solid[1] and gas-liquid[2] chromatography, a spectacular subtraction property has been observed with a specially treated silica gel column. This column selectively retained isoalkyl and cyclic paraffins but allowed normal paraffins, olefinic and aromatic hydrocarbons to pass through with symmetrical and sharp peaks. The authors are not aware of any stationary liquid, adsorbent or other column material having this unique selectivity. Of course, hydrocarbon type discriminating columns[3–7] are quite known for normal paraffins, aromatics, olefins and acetylenes.

Experimental

A commercial silica gel, 60/80 mesh, was cleansed with hot concentrated hydrochloric acid until no yellow colouration was present and then oven-dried at 120°C for 4 hours. It was treated with an aqueous solution of potassium hydroxide, dried under a UV-lamp to give 1.02 g. KOH/g. SiO_2 and was then packed in a $\frac{1}{4}''$ O.D. copper tube which was connected to a gas chromatograph (Hy-Fi 600C, Varian Aerograph) equipped with a flame ionization detector. Argon carrier gas was passed at 120°C. When the recorder base line was stable and linear, 1μl each of a few saturated hydrocarbons of different types followed by 10μl of pyridine were injected. None of these solutes were eluted. The contents of the $\frac{1}{4}''$ O.D. tube were taken out and given a final coating of 15.6 w/w per cent (on the basis of bare silica) glycerol in methanol by the evaporation technique. This support was dried at 100°C for 1 hour and then packed in a $3' \times 1/8''$ O.D. copper tubing. Another similar column was made with Chromosorb W, 60/80 mesh, treated exactly the same way as the silica gel. 10 to 100 μl of vapours of each solute were injected with a 1 ml gas-tight Hamilton syringe.

Results and Discussion

The acid-washed and dried silica gave a surface area of 375 m^2./g. by the BET nitrogen adsorption method. The retention behaviours of different types of hydrocarbons from the coated silica support column have been given in Table 1. The column temperature was 120°C and argon carrier gas flow was 14 ml./sec.

Under similar conditions of operation and column dimensions as above, all the compounds in Table 1 were irreversibly retained by the starting silica gel, but were eluted from the treated Chromosorb W. It is, therefore, evident that the extraordinary selectivity of the treated silica gel is not directly due to the coating chemicals or the starting silica gel, but to a new type of retentive forces imparted on the silica gel as a result of post-treatments. Probable changes on silica gel are on the bound and free silanols or on the three-dimensional pore structure or both. The elution of polar solutes, like olefins and aromatics, indicates that the surface hydroxyls of silica were deactivated by reaction during

TABLE 1—ELUTION CHARACTERISTICS OF DIFFERENT HYDROCARBON TYPES FROM THE COATED SILICA SUPPORT COLUMN

Compound	Retention Time, min.
n-pentane	1.00
n-hexane	1.60
n-heptane	2.75
n-nonane	9.50
n-decane	18.57
2-methylheptane	no elution
2, 3-dimethylbutane	no elution
2, 2-dimethylhexane	,, ,,
2, 4-dimethylhexane	,, ,,
2, 2, 4-trimethylpentane	,, ,,
Cyclopentane	no elution
Cyclohexane	,, ,,
Methylcyclohexane	,, ,,
1-cis-2-dimethylcyclohexane	,, ,,
2-methylpentene-1	1.87
Octene-2	6.23
Cyclohexene	2.00
Benzene	2.50
Toluene	4.88
Ethylbenzene	9.35
Ortho-xylene	11.32

post-treatments, because the retentive mechanism of π bonded solutes are known to be predominantly governed by the strongly reacting silanols[8].

The development of molecular sieving property on the silica gel is also a possibility. However, no known molecular sieve posseses the type of selectivity observed in the present investigation. This selectivity is just anti to Linde molecular sieve 5 Å. Non-existence of theoretical and experimental study in this area precludes any definitive statement on the invocation of the hypothesis of molecular sieving property on the silica for this special selectivity. Assuming that the treated silica gel is acting as a molecular sieve, a thorough investigation of this phenomenon will shed new light into the understanding and technology of molecular sieving action. Moreover, this modified silica adsorbent will have important practical applications in analytical and industrial separations.

When an adsorbent is prepared in presence of a particular compound which is later driven off, a tailored adsorption site is generated on the adsorbent which preferentially adsorbs the same compound when used as a column material. This phenomenon of specific adsorbent introduced by Dickey and Pauling[9] may be relevant to the present study, because, in-between the stages of post-treatments of the silica gel we had to make several injections of solutes in order to check the suitability of the final product.

It needs mentioning that the subtraction property of silica gel was lost after some 300 injections of solutes and attempts to regeneration did not succeed. The colour of the used silica gel was found to change from white to brownish yellow. For successful preparation of the silica gel support, it is essential to follow strictly the exact conditions and methods of treatment in proper sequence.

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Low-Angle X-Ray Study of Humic Acids

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Low-angle scattering of humic acids from different sources has been interpreted as due to micro-pores in the macro-structure of the substance. Their pore sizes have been estimated.

It is well-known that soil organic matter, besides being a nutrient to the plants and playing an important role in the binding of clay particles, has a fundamental effect on the physical properties of the soil. Soil organic matter increases air, vapour and water-holding capacities, and also chemical properties like exchange capacity. The micro-pores in the organic matter hold water by capillarity. Biggar and Nielsen[1] have discussed how the micro-pore structure of the soil leads to solute mixing due to the flow-velocity distribution during leaching of soil column. Rose[2] has shown that an increase in porosity will cause an increase in vapour diffusivity and an increase in vapour sorptivity, though this will depend on the complexity of the micro-pore space. Obviously, these properties are related to pore size provided by humus particles in the organic matter.

According to the present concept, humic acids are believed to be formed by a complicated process of oxidation, condensation and addition reactions from compounds of polyphenolic and/or quinonoid character. That is why they are best described as an amorphous and irregular hetero-polycondensates in dry condition. They have a basic structure of hexagonal benzene ring in graphite-like arrangement with side chains. Riley[3] and Kasatochkin[4] et al have observed that the different ranking corresponds to the condensation of increasingly graphite-like lattices with decreasing number of side chains, and they have calculated that the number of benzene rings varies between 1 and 10 in humic acids. Thus, small crystallites of humic acids exist in soil as an agglomeration having varying molecular weight of the order of a few thousand units consequently of varying sizes and composition. The pore size of such an agglomeration of humic acid particles is related to the physical and chemical properties of the soil. Therefore, an attempt has been made here to determine the pore sizes of a few humic acids extracted from different sources.

Experimental

Four samples have been taken for the present study. The details of their preparation are given below:

(1) *Humic Acids From Coal:* Vitrain was digested first with (N) KOH solution. It was precipitated with hydrochloric acid and filtered. The residue was washed free of hydrochloric acid and potassium chloride and then dialized, Thus, the regenerated humic acids were dried at 60°C in an electric oven.

(2) *Humic Acids From Soil:* This was a Swiss** make sample extracted from the soil.

(3) *Humic Acids From Amraoti (Maharashtra):* It was prepared by treating the soil with sodium carbonate solution followed by acidification and electrodialyses. The details of preparation have been described elsewhere[5].

(4) *Humic Acids From Marine Deposit (Indian West Cost Sediment):* It was prepared in the same way as (3).

To record their low-angle x-ray scattering, the Kieseig camera of Reich Seifert-make was used. The specimen was in the form of a plate of nearly 1 mm. thickness. The x-ray beam was collimated by a combination of

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**obtained from Fluk A. A. G., Switzerland

four slits of diameters 0.7, 0.8, 0.7 and 1.0 mm. A beam catcher of 2.5 mm. diameter was used to receive the primary beam. The film to specimen distance was kept at 99.34 mm. The exposure was taken with filtered CuKα radiation at 40 KV and 20 mA on Philips PW/1010 set. The camera was evacuated throughout the time of exposure. A blank exposure was taken under identical conditions. It revealed no scattering indicating that the low angle scattering observed earlier was only due to the specimen. Films were microphotometered to obtain the density of blackening. The microphotometric traces are shown in Fig. 1.

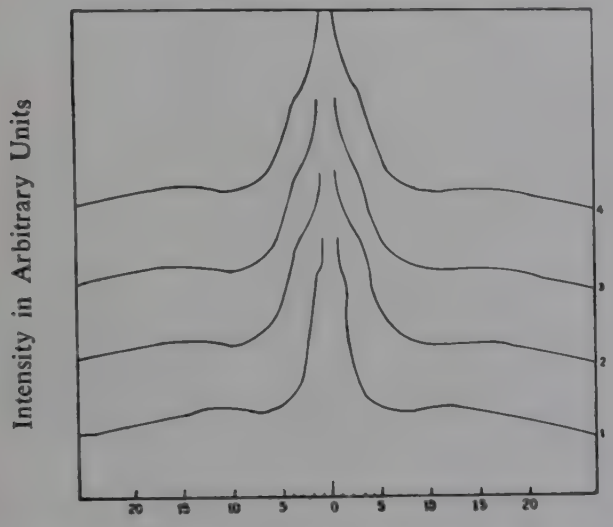

Fig. 1—Microphotometric Trace of Low-Angle Scattering of Humic Acids.

1. Humic Acids from Vitrain
2. „ „ „ Soil (Swiss make)
3. „ „ „ Amraoti (Maharashtra) Soil
4. Humic Acids from Vitrain Marine Deposits (Indian West Coast).

Results and Discussion

Debye[6] et al have shown theoretically that the low-angle x-ray scattering of a material is due to the changes in electron density introduced by the inhomogeneities in it. That is to say, empty space and matter inside the material will give rise to micropores and consequently, change in electron density. For such material Zhdanov[7] et al derived a relation for the calculation of average radius of pores, R, as follows:

$$R = \frac{0.32\lambda}{\phi \text{max.}}$$

where λ is wave length of x-ray beam and ϕ max., the angle of scattering where the intensity is maximum. Using the above formula, Porai-Koshits[8] et al calculated the radius of pores of some vitreous substances. They compared these values with electron microscopic measurements and found that the agreement was good within experimental error. Therefore, we also have used the same relation for the calculation of radii of micropores in our present work. The values thus obtained are given in Table 1.

TABLE 1

Name of the sample	(i) Humic acids from Vitrain	(ii) Swiss-make humic acids from soil	(iii) Humic acids from Amaraoti soil	(iv) Humic acids from marine deposit
Radius of Pore	23.7 Å	16.4 Å	16.4 Å	14.2 Å

From the above results, it is seen that soil humic acids have more or less the same value which is smaller than that from coal. This suggests that the soil humic acids are less homogeneous as compared to the humic acids extracted from coal. This is further substantiated by the microphotometric traces of humic acids prepared from soil showing steep fall in the low angle scattering intensity which indicates that the scattering particles are at farther and regular distances, whereas the microphotometric trace of humic acids from soil showing continuous scattering indicates that the scattering particles are closer and at random distribution.

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Estimation of Phosphate: A Rapid Polarographic Method

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A rapid polarographic method has been devised for estimating phosphate in the concentration range 4×10^{-1} to 1.5×10^{-6}M, using a homogeneous mixture of isobutanol, perchloric acid, water and hydrogen peroxide as a supporting electrolyte. The effect of various interfering ions on these estimations has been studied.

Object and Scope

Rock phosphate is a raw material for phosphatic fertilizers. However, before assessing its nature and processing technique the estimation of its phosphatic content is of utmost importance. So far, either gravimetric[1,2] or colorimetric[3,4] methods were used which are often tedious, time-consuming and involve a lot of interferences. Recently, Asaoka[5] has described a polarographic method for the estimation of phosphates, using a homogeneous mixture of isobutanol [$(CH_3)_2$ $CHCH_2$ OH], perchloric acid, water and hydrogen peroxide as a supporting electrolyte. He explored the positive potential region and observed a maxima at +0.2 v, the height of which was directly proportional to the concentration but his range of estimation was very low, viz. 2×10^{-5} to 3×10^{-7}M. In higher concentrations, this method was not suitable and hence it could only be used in the estimation of phosphate in steels (containing 0.03 per cent phosphorus). This, however, failed in the case of rock phosphates containing 6-45 per cent P_2O_5.

The present studies were, therefore, undertaken with a view to devise a rapid polarographic method for estimating phosphates in a wider range of concentration. This paper records observations leading to the estimation of phosphate in the concentration range 4×10^{-1} to 1.5×10^{-6} M and study the effect of various interfering ions on these estimations.

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Experimental

The reagents used were of B.D.H. (A.R.) grade unless otherwise specified. Double distilled water was used for preparing all solutions. A stock solution of ammonium molybdate (Allied Chemicals) was prepared and used from time to time.

The supporting electrolyte was prepared by mixing 10 ml. of 20 vol. hydrogen peroxide (Merckozone product) to 1.4136 ml. of isobutanol (wt./ml. 0.802 g.), 3.03 ml. of perchloric acid (Proanalysi. Merck product) (by wt. 1.67 kg. = 1 l.) and making the volume to 200 ml. with double distilled water. 3.0 ml. of this solution were then diluted to 100 ml. and used as a supporting electrolyte in all the studies.

All the studies were made on an automatic recording Cambridge Univector polarograph (using D.C. polarography) with a dropping mercury electrode and a dipping annulus type cell. Oxygen-free dry nitrogen was bubbled through the solution to drive off any dissolved oxygen. The bubbling of nitrogen was stopped during recording; there was a vacuum over the solutions in the cell. The characteristics of the capillary were the same. The droptime in the S.E. at −0.06 V was 4.7 secs.

Triple-distilled mercury (B.D.H. product) was filled in the mercury column (D.M.E. reservoir) and the height of the reservoir was kept constant except during the diffusion control studies. All the studies were made at room temperature, and only pyrex and Jena glass vessels were used.

Mixtures of hydrogen peroxide and molybdate oxi-

dize mercury. In presence of mercury, a noticeable decomposition occurs in 10-15 min. depending upon the acid and reagent concentrations. For this reason, polarograms were recorded within 10 min. after insertion of the electrode. The decomposition could be eliminated for longer periods of time by collecting the d.m.e. under carbon tetrachloride or chloroform.

Results

Cell Mixture: 5.0 ml. supporting electrolyte + 0.1 ml. Mo^{6+} + 0.1 ml. of rock phosphate soln. + 1.3 ml. water.
Initial volume = 6.5 ml.

With the same supporting electrolyte and molybdenum and phosphoric acid concentrations, identical results were obtained.

Discussion

On recording the polarogram of Mo^{6+}, after deaeration, two well-developed maxima were observed (Fig. 1) at −0.47, −0.62 V respectively, followed by a diffusion wave having E1/2 = −0.94 V and irreversible in nature and a wave of hydrogen peroxide. However, on adding phosphoric acid and recording its polarogram, a maxima was observed (Fig. 2) at −0.06 V. and the two maxima due to Mo^{6+} disappeared. On adding increasing amounts of phosphoric acid, the height of the maxima was observed to decrease but after diluting it increased. The range of estimations was 1.55×10^{-1} to 1.8×10^{-6} M (Table 1).

On addition of surface-active agents, like gelatin, the

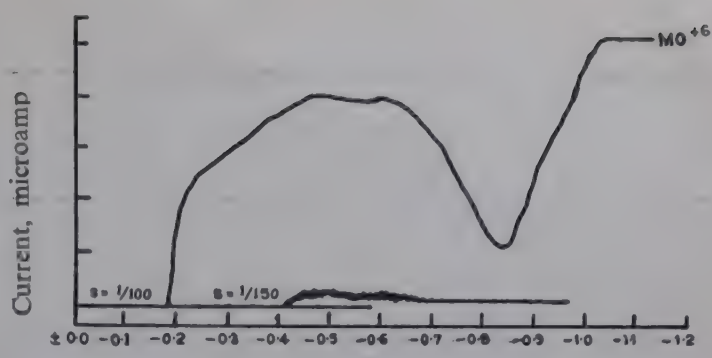

Fig. 1

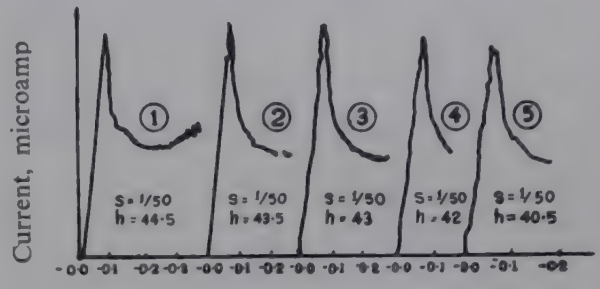

Fig. 2

maxima remains unchanged. Hence, the maximum current observed is due to kinetic phenomena rather than surface phenomena. A kinetic polarographic wave is obtained either when a reducible compound is in equilibrium with a non-reducible compound or when an oxidizing agent is reduced at the electrode and the reduction product reacts very rapidly with a second oxidizing agent in the solution. It has been found[6] that

TABLE 1—Relation Between Phosphate Concentration and Current

Sl. No.	Concn. of PO_4^{3-}M	Current, microamp.	Sl. No.	Concn. of PO_4^{3-}M	Current, microamp.
1	1.8×10^{-6}	7.500	16	0.0×10^{-3}	5.375
2	4.0×10^{-6}	7.325	17	1.25×10^{-3}	5.250
3	6.0×10^{-6}	6.975	18	1.53×10^{-3}	5.125
4	8.0×10^{-6}	6.750	19	1.60×10^{-3}	5.062
5	1.5×10^{-5}	6.600	20	2.00×10^{-3}	4.930
6	6.0×10^{-5}	6.300	21	3.03×10^{-3}	4.750
7	8.0×10^{-5}	6.250	22	4.47×10^{-3}	4.625
8	0.0×10^{-4}	6.025	23	5.88×10^{-3}	4.563
9	2.0×10^{-4}	5.950	24	7.24×10^{-3}	4.375
10	4.0×10^{-4}	5.875	25	8.57×10^{-3}	4.313
11	6.0×10^{-4}	5.800	26	9.85×10^{-2}	4.250
12	0.0×10^{-3}	5.650	27	1.11×10^{-1}	4.188
13	3.0×10^{-3}	5.550	28	1.36×10^{-1}	4.125
14	6.0×10^{-3}	5.425	29	1.50×10^{-1}	4.050
15	8.0×10^{-3}	5.400	30	1.55×10^{-1}	4.020

N.B.—Initial Concentration of Ammonium Molybdate: $1.53\times10^{4-}$M

TABLE 2—ANALYTICAL RESULTS

Sample number	Height of maxima, cm.	Sensitivity	Current, microamp	P_4O_5, %	
				Observed	Theoretical
CMEJ/277	36	$\frac{1}{50}$	4.500	9.6	9.5
CMEJ/121	33	$\frac{1}{50}$	4.125	41.1	39.5

molybdate in acid medium reacts with hydrogen peroxide forming a peroxy compound which is reduced.

$$MoO_4^{2-} + H_2O_2 \longrightarrow MoO_5^{2-} + H_2O \quad (1)$$

$$MoO_5^{2-} + 2H^+ + 2e \longrightarrow MoO_4^{2-} + H_2O \quad (2)$$

In presence of phosphate, the mechanism for the kinetic current is presumably caused by the reduction and reformation of a peroxyphosphomolybdate. Assuming that the mechanism for the molybdate kinetic wave is explained by equations (1) and (2), the kinetic current according to Brdicka[7] et al is given by

$$i_k = 2F\,\mu\,q^K\,10^{-3}\,[H_2O_2]\,[\text{Phospho-molybdate}],$$

where F is the Faraday, μ the thickness of layer in which reaction (1) is presumed to occur, q the average area of the surface of the mercury drop, K velocity constant for reaction (1) and i_k is the kinetic current in microamps.

This equation indicates that the kinetic current should be a linear function of phosphomolybdate concentration. Linear relationship is found to exist in the region 1.8×10^{-6} to 2×10^{-5} and 2.1×10^{-5} to 1×10^{-2} M concentrations separately. The deviations are due to different degrees of association of phosphomolybdates.

Addition of NO_3^{1-}, CO_3^{2-}, SO_4^{2-}, ClO_4^{1-}, F^{1-}, $C_2O_4^{2-}$ and tartarate do not have any effect on the height of maximum. Chloride, however, interferes strongly if present in more than 0.2 per cent quantity.

Estimation With Rock Phosphate Samples

A well-powdered and thoroughly-mixed sample of rock phosphate was weighed and digested with perchloric acid on a hot plate for 40 min. The solution was cooled, filtered and the residue washed with 5 ml. aliquots of perchloric acid (dil.) three times. The volume of the solution was made up and a 0.1 ml. aliquot of this solution polarographed as usual. The height of the maxima in microamperes gave the concentration of PO_4^{3-} in solution from comparison with the calibration curve. (The results of the two samples analysed are given in Table 2). Further work is in progress.

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Studies on Broken Valve Plate

By

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A strain-induced shift in the Curie point of iron has been observed in a broken valve plate of a hyper compressor. The failure has been found to be due to localized centres of large lattice strain coupled with cyclic stresses suffered by the compressor.

Valve plates of a hyper compressor from an ammonia plant of the FCI Ltd. were found to give way during the course of operation. In this communication attempts have been made to find out the cause for the same, using x-ray, electron microscopy and thermomagnetic techniques.

Spectro-chemical analysis of the plates showed the presence of chromium (2 per cent), manganese (0.5 per cent) and molybdenum (0.25 per cent). Total carbon content was estimated to 0.74 per cent by chemical analysis.

X-ray diffraction data of the bulk sample revealed the presence of only α–Fe phase. But the material extracted from the bulk sample showed the presence of the carbide of the type $M_{23}C_6$, where M stands for iron, chromium, manganese, molybdenum or their combinations (Table 1). To obtain the carbide, the bulk sample was treated with *aqua regia*, and the insoluble material was filtered, washed and dried. The diffraction patterns are reproduced in Fig. 1. A back reflection photograph of the polished and etched sample showed line broadening at the high angle side of diffraction.

TABLE 1—X-ray Diffraction Data

Bulk Material		α-Fe ASTM, 6-0696		Extracted Carbide		$(Cr, Fe, W, Mo)_{23}C_6$ ASTM, 5-0721	
d (Å)	I/I_1	d (Å)	I/I_1	d (Å)	I/I_1	d (Å)	I/I_1
2.043	vs	2.027	100	2.805	vw		
1.444	w	1.433	19	2.737	vw		
1.175	ms	1.170	30	2.532	vvw		
1.015	w, br	1.013	9	2.364	w	2.375	80
				2.173	w	2.168	60
				2.043	s	2.044	100
				1.876	vw	1.878	60
				1.794	vw	1.796	60
				1.771	vvw	1.680	60
				1.590	vvw	1.602	40
				1.490	vw		
				1.287	w	1.288	60
				1.252	m	1.252	80
				1.228	w	1.227	60
				1.166	vw	1.166	60
				1.084	ms	1.084	100
				1.068	w	1.068	40

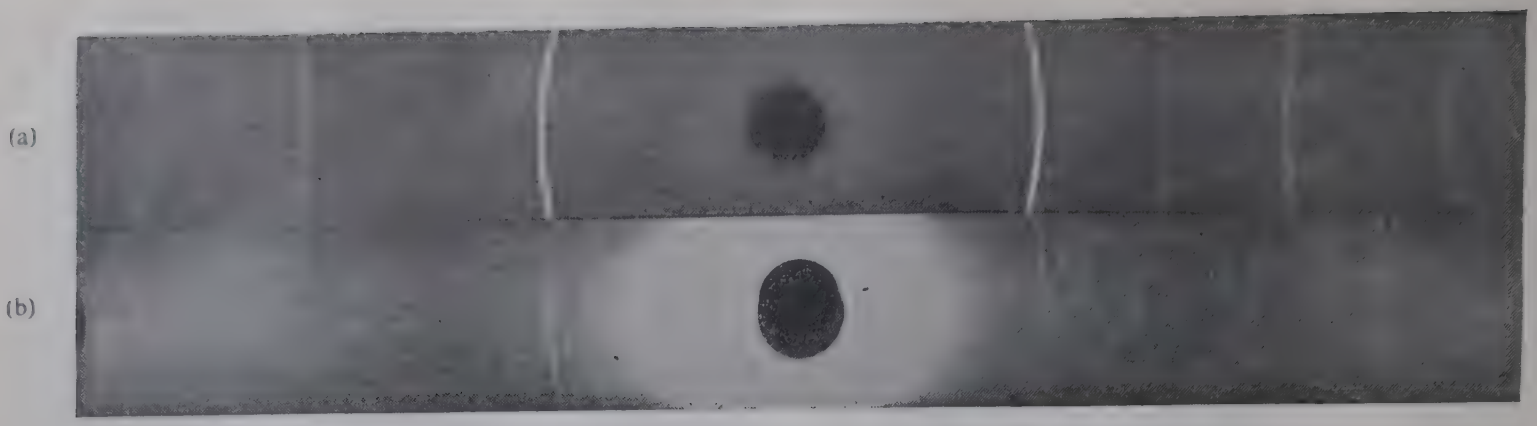

Fig. 1—X-Ray Diffraction of (a) Bulk Material (b) Extracted Carbide taken with FeK α, 5.76 cm. dia.

Fig. 2—Electronmicrograph of the valve plate (× 15,000).

Electron microscopic observation of the sample showed coarse carbide precipitation in a ferrite matrix (Fig. 2). Thermomagnetic study on the bulk sample showed two Curie point transitions (Fig. 3), one at 560°C and another at 740°C. The carbide, extracted from the bulk sample, was found weakly magnetic and did not show any Curie point transition. Both the Curie point transitions in the bulk sample were reversible and could be observed in the cooling curve after heating the sample upto 800°C. On heating the sample upto 840°C, the height of transition at 560°C decreased in the cooling curve.

The Curie point transition observed by thermomagnetic studies at 740°C is characteristic of α-Fe, but the transition at 560°C is difficult to explain as x-ray study did not show the presence of any phase other than carbide. The transition cannot be due to the magnetic oxide Fe_3O_4 (Curie point 575°C) as the concentration of Fe_3O_4 required to produce the observed magnitude of the drop in magnetic moment would certainly be detectable by x-ray diffraction. Similar arguments hold for the possibility of ascribing the transition to a precipitated alloy phase formed between Fe and the other metals, as the lowering of the Curie point of α-Fe from 775 to 740°C itself indicates that the other metals present are dispersed in the bulk matrix. That it is not due to the carbide, is already confirmed by studying thermomagnetically the carbide particles isolated from the bulk material.

To explain this anomalous phenomenon, we put forward the hypothesis that the carbide crystallites had induced a lattice distortion in the α-Fe phase in the regions immediately surrounding them. Both the α-Fe

Fig. 3—Thermomagnetic curve of the bulk material.

and $M_{23}C_6$ carbide belong to the cubic class with a_o (Fe) = 2.8664 Å[1] and a_o (Carbide) = 10.659 to 10.53 Å[2] depending on the nature of the metal M. It may be observed that $4 \times a_o$ (Fe) = 11.4656 Å, which is not much different from the lattice dimension of the carbide. It is, therefore, reasonable to assume that during the formation of the carbide crystals, packing and strength of the crystalline field had compelled the lattice dimension of the α-Fe crystals at the grain boundaries to shrink in order to match with that of the carbide. This would have caused different amounts of lattice strain in the overall ferrite structure which, in fact, was shown by the line broadening of the 220 reflection. The maximum distortion involved is small, of the order of 10 per cent only, but is sufficient to alter the degree of ferromagnetic exchange interaction locally and hence to alter the Curie point also. The amount present is significant from the point of view of magnetic measurements, but is still too small to be detectable by x-rays.

The net effect is the production of highly localized centres of large lattice strain. This stress concentration around the carbide particles leads to material failure under cyclic stresses suffered in the compressor.

The strain is expected to be relieved on annealing to sufficiently high temperature. The observed decrease in the height of the transition step on heating the sample above 840°C is an indication that the assumption is valid.

Acknowledgements

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Determination of Some Trace Impurities in Ammonium Bicarbonate by Atomic Absorption Spectrophotometry

By

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A simple method for the estimation of trace impurities in ammonium bicarbonate (ABC) has been developed. A sufficient quantity of the sample is decomposed in hot water and five trace elements, viz. iron, copper, manganese, zinc and magnesium, have been estimated quickly and accurately by using atomic absorption spectrophotometer.

Various methods are available in literature for the estimation of a number of elements in fertilizers and raw materials by atomic absorption spectrometry. McBride[1] determined copper, iron, magnesium, manganese and zinc in commercial fertilizers and raw materials by this technique. As the amount of these elements was appreciable in his samples, he followed a simple dilution method for sample preparation. In addition to above, Allan has determined copper[2], iron and manganese[3] and zinc[4] in fertilizers. In ABC the impurities are present

in a very low concentration, so a simple decomposition method for concentration has been utilized here for the determination of iron, copper, manganese, zinc and magnesium.

Experimental

Equipment: A Perkin Elmer Model 303 atomic absorption spectrophotometer with a burner nebulizer for air-acetylene flame was used. The spectrophotometer was equipped with a digital concentration readout accessory (DCR-1). The hollow cathode lamps used were also of Perkin-Elmer make.

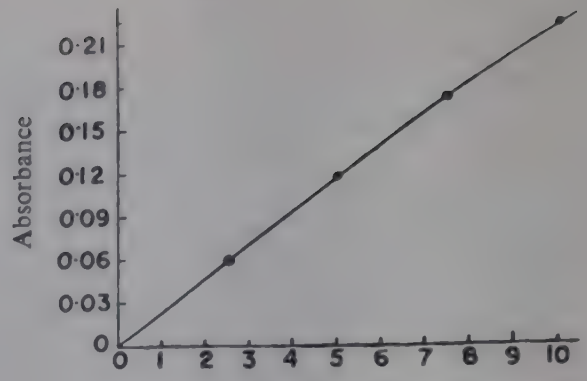
Sample Preparation: Eight different ABC samples were collected for the present work. As the content of elements under investigation was very low, preconcentration of the samples in solution was necessary.

For estimation of iron, copper, manganese, zinc and magnesium, 20.0 g. of ABC samples were weighed in 100 ml. conical pyrex flasks and 50 ml. of double distilled water was added to each flask. All the eight samples were gently heated on a hot plate for about 30 min. and allowed to decompose completely. When about 20 ml. of solutions were left over, 1 ml. of hydrochloric acid (AnalaR) was added in each solution and heated for a few minutes. The volumes were made up to 25 ml. and the acid strength in each sample was maintained at about 0.5N; these were kept in polythene bottles.

Standard Solution: Stock solutions containing 0.1 per cent of iron, copper, manganese, zinc and magnesium were prepared from GR/AnalaR quality of salts. From these solutions, a set of working standards was made for each element. The hydrochloric acid strength was kept 0.5N in the final working standards.

Procedure: The instrumental conditions for the different elements were set as given in Table 1. 0.5N hydrochloric acid was run as a blank for zero adjustment. The standard and sample solutions were aspirated and corresponding absorbance values were read from DCR-I directly for iron and zinc, whereas in the cases of copper, manganese and magnesium expanded scales were used and corresponding percentage absorptions were noted.

Analytical curves for iron, and zinc (Figs. 1 & 4) were drawn between concentration of the elements and their corresponding absorbance values. In case of copper, manganese and magnesium, the curves (Figs. 2, 3 & 5) were plotted between the concentration and percentage absorption. The values of the elements (Table 2) were determined from the above curves.



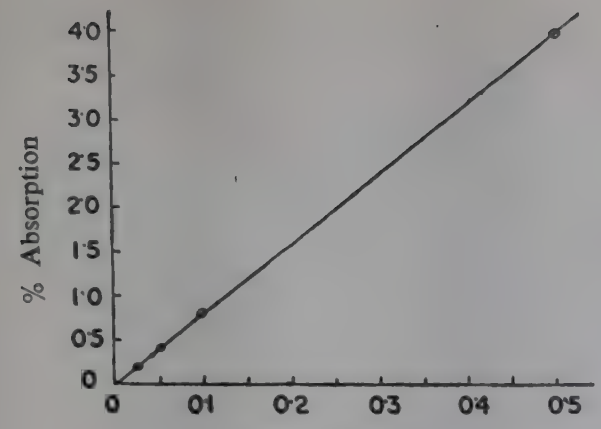
Iron, ppm.
Fig. 1

TABLE 1—Experimental Conditions

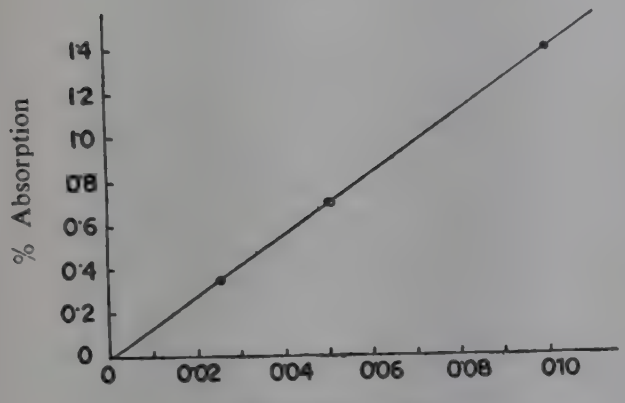
Element	Fe	Cu	Mn	Zn	Mg
Wave length, Å	2483	3247	2795	2138	2852
Slit width, mm.	0.3	1.0	1.0	3.0	3.0
Source, mA	20	15	15	15	6
Scale expansion	—	X10	X5	—	X2
Meter response/noise suppression	2	2	3	3	2
Flame	Oxidizing	Oxidizing	Oxidizing	Oxidizing	Reducing
Pressure, psi					
Air	30	30	30	30	30
Acetylene	8	8	8	8	8
Flow-meter Reading					
Air	9.0	9.0	9.0	9.0	8.0
Acetylene	9.0	9.0	9.0	9.0	9.0

TABLE 2—Trace Elements in Ammonium Bicarbonate Samples, ppm

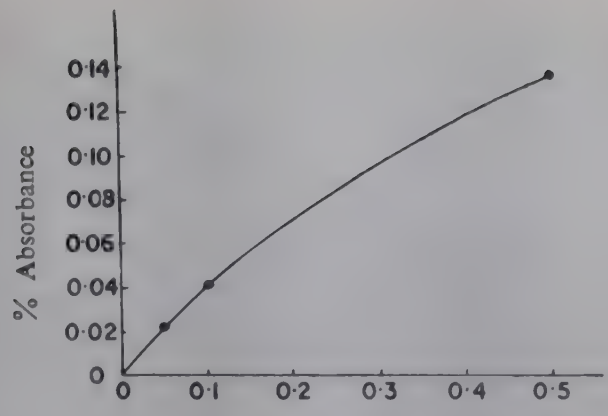
Sample No.	Fe	Cu	Mn	Zn	Mg
1.	4.06	0.04	0.06	Not detected	0.01
2.	5.56	0.12	0.05	"	0.06
3.	5.56	0.08	0.08	"	0.04
4.	4.20	0.12	0.03	"	0.09
5.	3.87	0.18	0.04	"	0.09
6.	8.62	0.07	0.04	0.02	0.04
7.	7.25	0.07	0.06	0.11	0.04
8.	2.50	0.08	0.03	0.09	0.12



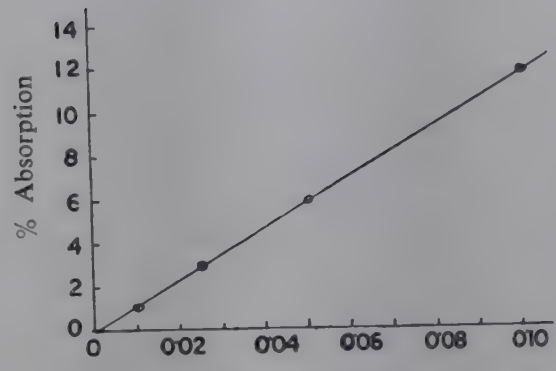
Copper, ppm.
Fig. 2



Manganese, ppm.
Fig. 3



Zinc, ppm.
Fig. 4



Magnesium, ppm.
Fig. 5

Discussions

The concentration method by decomposition of the samples in hot water, used for the present work was simple and less time-consuming. This was found to be quite satisfactory in case of ABC (which totally decomposed in hot water) wherein the trace elements were concentrated without increasing the solid content in the solution which would have affected the determination by atomic absorption spectrophotometry. Matrix effect was studied in case of iron determination by comparing the values obtained from standard calibration method and addition method. The values were found to be same showing the absence of any matrix effect.

Acknowledgement

Thanks are due to Sri A. C. Banerji for assistance in this work.

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Estimation of Phosphorus in Rock Phosphate by Flame Emission Technique

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Phosphorus has been estimated in rock phosphate by a flame photometric method employing the depressing effect of phosphorus on the intensity of calcium oxide band (622 mμ) in the coal gas flame. The cation interferences were removed by a cation exchange resin and an addition method instead of the calibration method was used. The phosphorus interference curve with calcium showed a tendency to bend towards the concentration axis. This curvature was removed by adding an element having a low ionization potential, viz. potassium (1000 ppm). The results are in good agreement with those obtained from other methods.

There are methods for estimation of phosphorus by flame emission technique. The direct methods are mostly restricted to the measurement of intensity of molecular species of phosphorus as the principal atomic lines of phosphorus lie in vacuum ultraviolet (1775, 1783 and 1788 Å) and are, therefore, outside the range of the conventional atomic emission, absorption and fluorescence instruments. Brite[1] estimated organic phosphorus by measuring phosphorous continuum at 540 mμ. Davis[2] et al also estimated phosphorus in the oxyhydrogen flame by the same method.

Recently, Dagnall[3] et al have established the method for the estimation of phosphorus, based on the measurement of molecular emission intensity of P_2 band at 528 mμ in nitrogen-hydrogen cool diffusion flame. The detection limit obtained was 0.1 ppm phosphorus in aqueous solution. The P_2 band intensity is effected by cations which were removed by the cation-exchange resin.

The indirect method of estimation is based on the observation that phosphorus depresses the calcium emission and is linear upto a point where the calcium to phosphorus ratio is 2 to 1. Leyton[4] has used this relationship for the correction of calcium results in the biological samples which suffer interference due to the presence of phosphate. Dipple[5] et al have estimated the phosphorus in rock phosphate by removing all the cations from the sample by a cation exchanger and employing the depression on fixed calcium concentration in air-acetylene flame. Our method is primarily based on the Dipple's method, but instead of usual calibration curve an addition method is used which is very similar to the standard addition method, using coal gas instead of air-acetylene flame.

Interference and Ionization

Calcium suffers from interferences due to the presence of anions and cations. The cationic interferences are not of very much interest in this problem because they are removed by cation-exchange resin. The phosphorus interference on calcium band at 622 mμ is shown using air-acetylene flame (Fig. 1) and coal gas flame (Fig. 2 a). In air-acetylene flame, the interference of

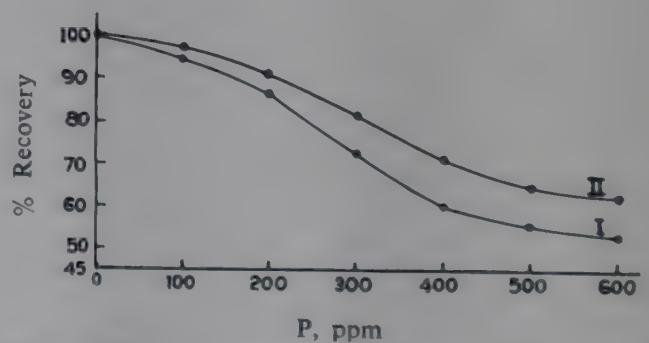

Fig. 1—Study of Phosphorus Interference on 1000 ppm of Calcium in Air-Acetylene Flame.
I—C_2H_2 pressure 180 mm
II— " " 90 "

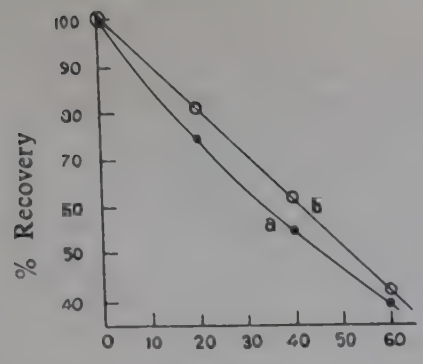

Fig. 2—Phosphorus Interference on Calcium using Coal Gas.
a—200 ppm of Ca
b— „ „ „ Ca+1000 ppm of K

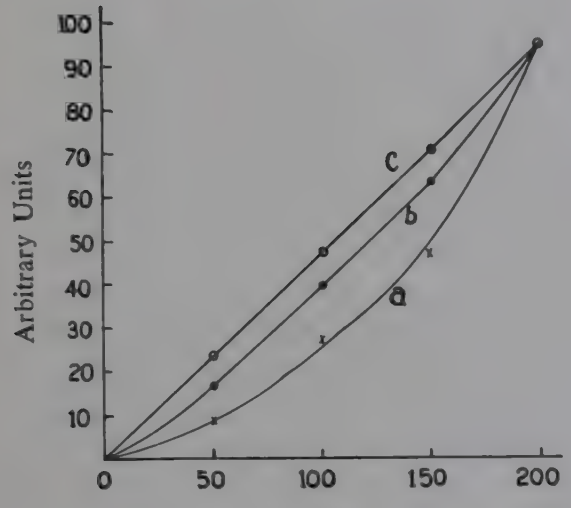

Fig. 3—Calibration Curve of Calcium in Coal Gas.
a—without Na and K
b—with 1000 ppm of Na
c— „ „ „ „ K

phosphorus at lower values is not very significant. In case of coal gas, a little bend was observed at higher concentration of phosphorus (Fig. 2a). A similar bend was also observed in calcium calibration curve in the same flame (Fig. 3a). The phosphate interference is due to the formation of calcium phosphate in the flame which does not dissociate completely. This bend can be attributed to ionization, as at higher phosphorous concentration less calcium atoms are available for emission[6]. This ionization can be inhibited by adding an easily ionized metal to the sample solution. Potassium and sodium were tried (Fig. 3b & Fig. 3c) and it was observed that 1,000 ppm of potassium removes the curvature in calcium calibration curve but in case of 1,000 ppm of sodium slight bend still remains. For finding out the correct concentration of potassium, the effect of a varying amount of potassium as potassium chloride was investigated (Fig. 4). Phosphorous interference was also observed in coal gas at 200 ppm of calcium with 1,000 ppm of potassium (Fig. 2b). The curve obtained in this case was a linear one and can be used for the estimation of phosphorus either by a calibration curve or by the addition method.

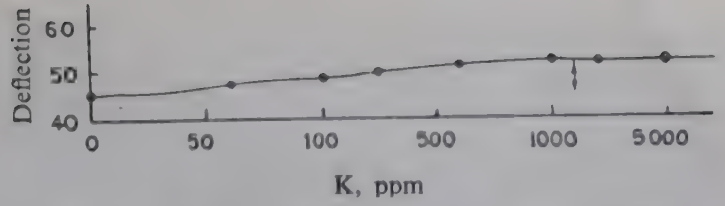

Fig. 4—Effect of Potassium on 200 ppm of Calcium.

Addition Method

The conventional addition method[6] is widely used to eliminate the matrix effect and to attain a better accuracy. The method is valid when the relationship between the concentration and the intensity of the added element is linear. In the standard addition method, the curve converges to the negative side of the concentration axis. In present method the curve diverges from the negative axis as the calcium intensity decreases with the addition of phosphorus. Unknown values of phosphorus would, therefore, correspond to the blank deflection of calcium and can be estimated by extrapolating the curve to the negative side of the concentration axis (Fig. 5).

Reagents: (1) 2 per cent stock solution of calcium was prepared from calcium carbonate (AnalaR) in a minimum, amount of hydrochloric acid; (2) 2 per cent potassium stock solution prepared from potassium chloride (AnalaR); (3) 1,000 ppm. stock phosphorous solution prepared from di-sodium phosphate (AnalaR) after the cation separation by cation-exchange resin Amberlite IR-120 (H^+); (4) 2 per cent sodium stock solution prepared from sodium chloride (AnalaR); (5) 2,000 ppm. of calcium and 10,000 ppm. of potassium is prepared by suitably mixing (1) and (3) reagents; and

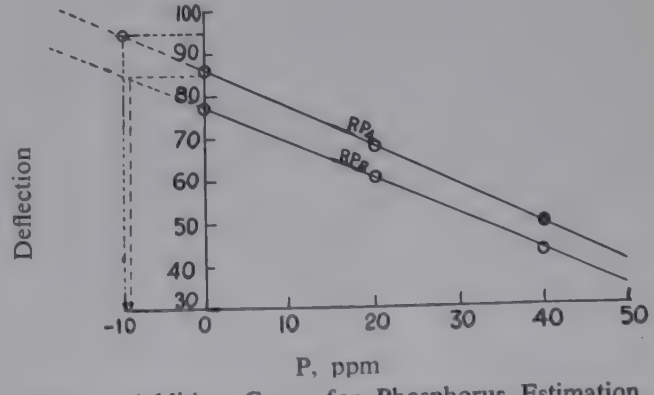

Fig. 5—Addition Curve for Phosphorus Estimation.

TABLE 1—DETERMINATION OF P_2O_5 IN ROCK PHOSPHATE

Observation	Sample No.	P in Working Sample, ppm.	P in Rock Sample, %	P_2O_5 in the Sample, %	Atomic Absorption Analysed Value* of P_2O_5, %	Deviation
1.	RP_1	9.75	12.19	28.04	28.05	−0.01
2.	RP_2	9.00	11.25	25.87	25.19	+0.68
3.	RP_3	9.00	11.25	25.87	25.75	+0.11
4.	RP_4	10.00	12.50	28.75	28.06	+0.69
5.	RP_{131}	13.60	17.00	39.10	39.02	+0.08

*Chemically analysed value.

(6) Amberlite IR-120 (H^+) prepared from sodium form resin by washing with 4N hydrochloric acid.

Sample Preparation: 0.1 g of finely ground sample of rock phosphate was digested in 10 ml. of concentrated hydrochloric and 5 ml. concentrated nitric acid. This was first gently heated for about 30 min. at a low temperature and then evaporated to dryness, and subsequently baked to dehydrate the silica. The residue was taken in 4 drops of concentrated hydrochloric acid, filtered, washed and the volume was made to about 50 ml. The solution was passed through a column of Amberlite IR-120 (H^+), which was washed with 50 ml. of 0.015N hydrochloric acid to avoid the precipitation of iron and aluminium phosphates as suggested by Samuelson[7] and then with di-ionized water to make the volume upto 250 ml. Four volumetric flasks of 100 ml. capacity marked A to D, were taken and in each 10 ml. of reagent No. 5 was transferred. In B, C and D, 20 ml. of cation-free sample was added. In C and D, 20 ml. and 40 ml. of 1,000 ppm. of phosphorus was added respectively. All the four samples contained 200 ppm calcium and 1,000 ppm of potassium. Among these A served as blank and B the unknown. The same procedure was followed for all the samples.

Instrument and Procedure: Dr. Bruno Lange's Standard model-I flame photometer equipped with a multiflex galvanometer and calcium interference filter having a band pass at 622 $m\mu$ was used. A burner atomizer for coal gas and acetylene were used. Coal gas was taken from the laboratory pipe line and acetylene from cylinders. The gases were passed through a venturi of 1 mm. diam. which was connected at both the ends with a U-shaped water manometer tube. The steady flame was achieved at 240 mm. water column which was the maximum pressure of the gas line. There were not many parameters available for change in coal gas, therefore all the observations were taken at the line pressure. The compressed air pressure was 0.6 kg/sq.cm. for coal gas but for acetylene it was adjusted to give steady flame. Standard procedure was adopted for aspirating the samples. For drawing the addition curve, the value of phosphorous was plotted as in the conventional addition method but against the corresponding calcium deflection. The value was determined with the help of the deflection for the blank by extrapolating the curve in the negative abscissal side.

Results and Discussion

The results obtained by the addition method are in good agreement with those obtained by the other methods. This method is simple and convenient when a less number of samples are to be analysed and minimizes the instrumental error arising due to the time factor (Table 1). The bend in the calcium calibration curve is not generally expected in low temperature flame and may be rectified by adjusting the fuel to the air ratio. In our case, the gas flow parameters were fixed, therefore, the different fuel studies were not possible. In the present condition 1,000 ppm. of potassium serve the purpose. The depression of calcium due to phosphorus is more in coal gas flame, therefore, lower detection limit can be obtained in this flame than the air-acetylene flame.

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Infrared Spectra of Chlorapatite

By

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The infrared spectra of mineralogical and synthetic chlorapatite, $Ca_{10}(PO_4)_6Cl_2$, over the range 4000-200 cm.$^{-1}$ are reported. The molecular symmetry T_d of the phosphate ion in chlorapatite is reduced to C_s. Chlorapatite does not show the presence of 635 cm.$^{-1}$ and 3578 cm.$^{-1}$ bands which are due to the hydroxyl groups showing that OH- group of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, have been replaced by Cl^- ions. The nature and extent of changes in vibration frequencies of hydroxyapatite with the substitution of Cl^- ion for OH^- are discussed.

Introduction

Apatites are crystalline solids typified by hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, a basic calcium phosphate. They are important substances both in the animal and mineral kingdom.

It is now possible to prepare an apatite with chloride in place of the hydroxyl ion, in which case the compound is known as chlorapatite. Chloride ion will replace hydroxyl chemically but it occupies slightly different *a* and *c* axes position from the hydroxyl ion. The unit cell dimensions of hydroxyapatite and chlorapatite are given in Table 1.

TABLE 1—UNIT CELL DIMENSIONS OF HYDROXYAPATITE AND CHLORAPATITE[1]

Sample	a-axis Å	c-axis Å	c/a
$Ca_{10}(PO_4)_6(OH)_2$	9.42	6.88	0.730
$Ca_{10}(PO_4)_6Cl_2$	9.63	6.78	0.704

The structure given by Hendricks et al[2]. for the hexagonal crystal chlorapatite, $Ca_{10}(PO_4)_6Cl_2$, has long been accepted as essentially correct. However, there is need of some new structural evidence to explain the decrease in *c* axis and an increase in *a* axis going from hydroxyapatite to chlorapatite.

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Experimental and Results

The infrared absorption spectra of mineralogical and synthetic chlorapatites have been compared with that of a synthetic sample of hydroxyapatite. The mineral specimen of chlorapatite was from Odergarden near Feset, Norway. The hydroxyapatite and chlorapatite specimens were synthetic materials.

The samples were ground in a small agate mortar to a fine powder. The KBr pellet technique was used to study the infrared absorption spectra. The spectra were recorded with a Beckman Infrared spectrophotometer IR-12. The frequencies and assignments for the absorption spectra of hydroxyapatite and chlorapatite are given in Table 2.

TABLE 2—FREQUENCIES (Cm-[1]) AND ASSIGNMENTS FOR HYDROXYAPATITE AND CHLORAPATITE

$Ca_{10}(PO_4)_6(OH)_2$	Mineral $Ca_{10}(PO_4)_6Cl_2$	Synthetic $Ca_{10}(PO_4)_6Cl_2$	Assignment
3578 w, sha	—	—	ν_SOH
1095 s	1095 s	1092 s	
1050 s	1082 s	1080 s	ν_3PO_4
1035 s	1040 vs	1045 vs	
962 w, sha	960 w	962 w	ν_1PO_4
635 w	—	—	ν_LOH
605 s	600 s	605 s	ν_4PO_4
568 s	560 s	570 s	
475 w	465 m	472 m	ν_3-ν_4=1045-570=475
425 w	415 w	425 w	ν_3-ν_4=1045-605=440
355 m	305 m	315	ν_2PO_4
255 w			

w=weak, sha=sharp, s=strong, m=medium, vs=very strong ν_L=librational, ν_S=stretching.

Discussion

The hydroxyapatite has two peaks at 635 and 3578 cm.$^{-1}$. The 635 cm.$^{-1}$ band has been assigned to the librational mode of the hydroxyl group in hydroxyapatite[3,4]. The band at 635 cm.$^{-1}$ was found to arise from proton motion due to the shift by about $1/\sqrt{2}$ upon deuteration from 631 to 455 cm.$^{-1}$. The librational motion is basically described as oscillatory or hindered motion of the protons[5]. This band (at 635 cm.$^{-1}$) is absent in chlorapatite. The absence of 3578 cm.$^{-1}$ band in chlorapatite (Table 2) is consistent with the high chloride contents of the samples which shows that most of the positions on the six-fold axis are occupied by chloride rather than the hydroxyl ions.

From the structure of chlorapatite, it is known that the only symmetry element possessed by the site occupied by the phosphate ions is a plane of symmetry perpendicular to the c axis. The phosphorus and two of the oxygen atoms lie in this plane, whilst the remaining oxygens are symmetrically placed above and below it. The site symmetry is C_s and consequently all the modes are infrared active and all the degeneracies are lost. The lowering of the symmetry of the phosphate ion from T_d to C_s causes ν_1, at 980 cm^{-1}. to become infrared active. It appears at 960 and 962 cm^{-1}. in mineral and synthetic chlorapatite, respectively. The normal mode ν_2 at 363 cm^{-1}. also thus becomes infrared active.

Two bands in the region 410 to 480 cm^{-1}. are not as intense as the other members of ν_4 in hydroxyapatite. They are assigned as the difference tones as the numerical values of their frequencies are close in magnitude to the difference between ν_3 and ν_4. Stutman et al[6] observed only one band between 410 to 480 cm^{-1}. region and excluded it from a ν_4 designation.

Acknowledgements

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An Economic Evaluation of Nitric Phosphates and Diammonium Phosphate Production

By

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This paper discusses mainly the production of various nitric phosphates and diammonium phosphate, and compares their production costs. A comparative study of diammonium phosphate production with imported intermediates has also been studied. An attempt has been made to determine the cost of N and P_2O_5 nutrients in nitric phosphate (sulphate recycle) and diammonium phosphate manufacture with either imported or indigenous phosphoric acid, and their relative economics under the present Indian conditions have been summarized. The present paper emphasizes that nitric phosphate (sulphate recycle) production is economically cheaper than diammonium phosphate production schemes.

The increasing demand of fertilizers is clearly related to the development of the agricultural sector which is the most prominent sector of economy and contributes significantly to the national income. It is imperative that agricultural sector keeps pace with other sectors for two important reasons, viz. the rapid growth in population and the current low level of per capita consumption of agricultural commodities. Hence, it is of utmost importance for judicious planning to enhance the fertilizer production capacity, in view of its growing demand. This is especially so for the phosphate fertilizers (when its anticipated demand is projected to about 2 million tonnes of P_2O_5/year by the fourth plan period).

Technology

The basic raw materials—rock phosphate and sulphur—for the production facilities of the phosphatics are at present imported. Till the deposits of rock phosphate in Rajasthan and Mussorrie are fully proved and their effective economic mining method found, and the sulphuric acid production from indigenous Amjhore (Bihar) pyrites or from natural or phospho-gypsum (by-product gypsum from wet process phosphoric acid) becomes promising and successful, these imports will continue.

P_2O_5 in the apatite in rock phosphate is the source of the nutrient of the phosphatic fertilizers. This P_2O_5 which exists in tricalcium form in the rock, is extracted and solubilized with acids to make the P_2O_5 available for plant. Processing of rock phosphate with acids—sulphuric, hydrochloric, nitric or phosphoric—is simple but controversy arises whether P_2O_5 in the end-product should be water-soluble or partially water-soluble or citrate-soluble. This controversy is due to apparently variable response of the plant to P_2O_5 of various solubility in the soils depending on the soil characteristics and environs.

P_2O_5 of the rock, in the different conventional manufacturing processes, can be released and fixed in the finished product either in the water-soluble form—ammonium phosphates or monocalcium phosphates—or in citrate-soluble, viz. dicalcium phosphate form or as a mixture of both.

The production methods for water-soluble phosphates are based predominantly on the use of sulphuric and phosphoric acids for treating the rock. This entails substantial amount of foreign exchange for the import of the basic raw material, viz. sulphur. In the nitric phosphate route, nitric acid instead of sulphuric acid is used, thus avoiding sulphur.

The molal ratio of CaO to P_2O_5 in the commercial phosphate rock varies from 3.4 to 4: 1. To break apatite by chemical treatments with acids, a minimum acidula-

tion mole ratio of acid to CaO of 1.8 is necessary in the extractor and as the proportion of acid becomes higher and rock less, the solubility of P_2O_5 increases. CaO/P_2O_5 mole ratio should be less than 2.3 in the manufacture of nitric phosphates to avoid reversion of the phosphate, ensuring that the phosphate compound should not be more basic than D.C.P. The fundamental feature and the technique involved in the nitric-phosphate process is the removal or conversion of calcium nitrate formed during reaction of rock with nitric acid.

The utilization of sulphuric and nitric acids for the solubilization in the conventional Sulphonitric process and subsequent ammoniation and granulation results in a low nutrient product (12.9: 12.9:0) with about 50 per cent water-soluble P_2O_5 in the product. Similarly, in Carbonitric process using nitric acid alone with successive carbonation, ammoniation and granulation produces a citrate-soluble product of only 16:14:0 grade.

In both the cases, the aqueous slurry contains inert materials viz. calcium sulphate and carbonate, because the calcium nitrate produced in the reaction tanks is converted to the above products, as the presence of the nitrate in the finished material is objectionable due to its poor keeping quality and its hygroscopic nature. The present study excludes the above products because of their low nutrient value.

In the Odda process, $Ca(NO_3)_2.\ 4H_2O$ formed during acidulation of rock with nitric acid is separated partly from the process stream by precipitation of calcium nitrate by cooling and centrifuging, the rest of it being converted to ammonium nitrate and dicalcium phosphate (about 60-70 per cent of total calcium is removed to get a 50 per cent water-soluble P_2O_5 product). The separated calcium nitrate salt is processed as fertilizer grade ammonium nitrate (33.5 per cent N) as such or as CAN (21 per cent N) as a by-product[1].

A modification of this process is the recycle of the converted ammonium nitrate from the separated $Ca(NO_3)_2.\ 4H_2O$ to the system (Odda-Kampka). Another modification is the conversion of calcium nitrate to gypsum by ammonium sulphate solution, removal of gypsum by filtration and recycling of ammonium nitrate solution resulting in a product of high water-solubility and wide range of grade formulations (Auby).

Another modification envisages the conversion of gypsum, filtered off from the slurry, to ammonium sulphate liquor (39 per cent) with ammonia and carbondioxide *in situ* and recycling of the solution to the reaction tanks together with nitric acid (53 per cent), filtrate phosphoric acid and ammonium nitrate solution. It is evident that nitric phosphate with sulphate recycle or Odda process completely eliminates the use of sulphur as against DAP which requires about 1 te of sulphur per te of P_2O_5 in DAP.

Phosphonitric nitricphosphate is obtained by reacting rock phosphate with nitric acid and phosphoric acid. The slurry is preneutralized and then fed to the ammoniation-granulation system. The product is of 20:20:0 grade and is 50 per cent water-soluble.

DAP is manufactured by neutralization of phosphoric acid (produced by reacting sulphuric acid with rock phosphate) with ammonia. The product is completely water soluble.

TSP is produced reacting phosphoric acid with rock phosphate. P_2O_5 in TSP is about 85 per cent water soluble. However, when urea is mixed with TSP to produce complex fertilizer, reversion of P_2O_5 to an insoluble form takes place. To make TSP suitable for mixing with urea, it is ammoniated partially. This, however, brings down the water-solubility of P_2O_5 to 50 per cent.

Due to the non-availability of sulphur, most of the European countries have diverted their attention to the nitric phosphates, without using sulphuric and phosphoric acids. Mostly they manufacture complex fertilizers by Odda-Kampa or Odda processes or sulphate recycle process producing upto 85 per cent water soluble P_2O_5 in the product.

Economics

This paper basically confines its study to a comparison of DAP (18:46:0), nitric phosphates by Odda process with 50 per cent water solubility P_2O_5 (20:20:0) grade, phosphonitric (20:20:0) product with 50 per cent water-solubility and the nitric phosphate (25.3:14.7:0) sulphate recycle which can make a product of water-solubility of P_2O_5 ranging from 30 to 95 per cent.

In recent years, one school of thought advocates import of intermediates, like ammonia and phosphoric acid, and production of DAP from these imported intermediates. The economics of production of DAP and phosphonitric using imported intermediates have also been included in the comparison.

The investments for the various schemes are estimated on the basis of preliminary designs and utilizing the know-how and latest cost figures available. The amount of expenditure envisaged under rupee financing for plants and machinery is on the basis of maximum indigenous availability at current level of fabrication

facilities. The foreign exchange component requirement on account of fees for process know-how and agreements has been kept to a minimum utilizing indigenous know-how to the maximum extent possible. The estimates towards departmental charges, erection, supervision and commissioning, etc. are based on a reasonable time schedule. The financing charges have been calculated on a debt-equity ratio of 1:1.

The plants have the same P_2O_5 capacity i.e. 92,700 te P_2O_5/yr. They are assumed to be located at the refinery and coastal region. The basis of calculation and unit costs of raw material and utilities are given in Tables 1 and 2.

The inference from Table 2 is self-explanatory. The DAP production with imported intermediates, though low in initial investment, has a higher recurring foreign exchange expenditure annually, higher cost of production and cost per tonne of total nutrient than those of the products from the Odda or sulphate recycle nitric phosphate processes.

Though the cost of production of a product is important to the manufacturer, the farmer is interested in the cost of fertilizer as delivered to his field. From the viewpoint of delivered cost to the farmers, nitric phosphate, in terms of per tonne plant nutrient, is markedly cheaper than the DAP for a marketing or consumption centre even beyond 2000 Km. from the producing plant,

TABLE 1—Basis of Calculation & Cost Elements

(*a*) Imported phosphoric acid, ammonia, sulphur and rock phosphate storage facilities are taken for 60 days.

(*b*) Indigenous naphtha, fuel oil storage capacities are of 7 days.

(*c*) The landed cost of imported ammonia, phosphoric acid, sulphur, rock phosphate are based on prevailing prices of Rs. 315/te ($ 40/te C & F), Rs. 1058/te P_2O_5 ($ 140 C & F), Rs. 420/te ($ 56/te C & F), Rs. 173/te ($ 22/te C & F) respectively.

(*d*) Naphtha, fuel oil and make-up gypsum prices are at Rs.138/te, Rs. 206/te and Rs. 30/te respectively.

(*e*) The cost of utilities, power, steam, cooling water, boiler feed water are taken at Rs. 60/MWh, Rs. 18/te, Rs. 0.15/m^3, Rs. 1/m^3 respectively.

(*f*) Sale prices of DAP(18:46:0), sulphate recycle nitric phosphate (25.3:14.7:0), Odda and phosphonitric nitric phosphates (20:20:0) are calculated at Rs. 946/te, Rs. 556/te and Rs. 580/te bagged respectively, assuming sale price of Rs. 1200/te N and Rs. 1500/te P_2O_5 unbagged existing in the market.

(*g*) Maintenance materials are taken @3 per cent of manufacturing facilities.

(*h*) Insurance and local taxes are taken @ 0.5 per cent of manufacturing facilities.

(*i*) Depreciation is calculated on the declining balance method and works out to about 9.5 per cent of total investment less initial working capital and spares.

TABLE 2—Investment, Cost of Production, Profitability Analysis etc. for Different Schemes

Sl. No.	Item	DAP SCHEME (18:46:0)				Nitric phosphate Scheme (25.3:14.7) (Sulphate Recycle)	Odda Scheme (20:20:0)	Phosphonitric Scheme (20:20:0)	
		Imported Ammonia Imported Phos. Acid	Imported Ammonia Indigenous Phos. Acid	Indigneous Ammonia Imported Phos. Acid	Indigenous Ammonia Indigenous Phos. Acid			Imported Ammonia Indigenous Phos. Acid	Indigenous Ammonia Indigenous Phos. Acid
1	2	3	4	5	6	7	8	9	10
1.	Erected cost of Plants, Rs. lakhs	236.78	1006.95	726.08	1496.78	3790.50	3699.35	2052.47	3196.97
2.	Total Off-site facilities, Rs. lakhs	220.50	247.80	202.65	220.50	913.38	787.50	609.00	560.70
3.	Working Capital and Spares, Rs. lakhs	245.89	281.38	243.17	278.23	317.00	309.05	376.29	353.96
4.	Financing Charges Rs. lakhs	24.61	53.76	41.02	69.84	184.00	167.86	106.32	143.90
5.	Total Investment, Rs. lakhs	727.78	1589.89	1212.92	2065.35	5204.88	4963.76 (incl. CAN Plant)	3144.08	4255.53
6.	Foreign Exchange Rs. lakhs	304.35	461.15	506.88	665.60	1825.50	1716.82	968.29	1484.98
7.	Nutrient Output: N, te/yr.	36,000	36,000	36,000	36,000	1,53,000	95,500 (CAN) 92,700 (N-P)	92,700	92,700
	P_2O_5, te/yr.	92,700	92,700	92,700	92,700	92,700	92,700	92,700	92,700
8.	Investment/te Nutrient Rs./te. yr.	565.00	1235.00	945.00	1610.00	2120.00	1770.00 (incl Nutrient for CAN)	1700.00	2300.00

(Continued on next page)

TABLE 2—INVESTMENT, COST OF PRODUCTION, PROFITABILITY ANALYSIS etc. FOR DIFFERENT SCHEMES *(Contd.)*

Sl. No.	Item	DAP SCHEME (18:46:0)				Nitric phosphate Scheme (25.3:14.7) (Sulphate Recycle)	Odda Scheme (20:20:0)	Phosphonitric Scheme (20:20:0)	
		Imported Ammonia Imported Phos. Acid	Imported Ammonia Indigenous Phos. Acid	Indigneous Ammonia Imported Phos. Acid	Indigenous Ammonia Indigenous Phos. Acid			Imported Ammonia Indigenous Phos. Acid	Indigenous Ammonia Indigenous Phos. Acid
1	2	3	4	5	6	7	8	9	10
9.	Cost of Production Rs./te.	727.30	766.92	735.96	777.92	329.00	304.32	437.47	428.65
10.	Cost/te. Nutrient Rs./te	1140.00	1200.00	1150.00	1220.00	825.00	765.00	1095.00	1070.00
11.	Cost/te Nutrient incl. 11% return on investment Rs./te.	1159.30	1286.00	1212.50	1349.00	991.00	983.00	1216.00	1258.00
12.	Distribution Charges Rs./te Nutrient	78.00	78.00	78.00	78.00	125.00	125.00	125.00	125.00
13.	Transportation Cost/te Nutrient (2000 Km distance as per 35A classification of goods Tariff Rates)	89.00	89.00	89.00	89.00	142.50	142.50	142.50	142.50
14.	Delivered Cost Rs/te Nutrient	1326.30	1453.00	1379.50	1516.00	1258.50	1250.50	1483.50	1526.00
15.	Profitability:								
	(*i*) Total Capital	50.30%	21.80%	31.90%	16.30%	27.00%	15.20%	20.60%	16.60%
	(*ii*) Equity Capital	118.00%	40.60%	65.00%	27.40%	47.00%	24.20%	36.80%	27.40%
16.	Pay-Back Period in Yrs.	1.82	3.48	2.60	4.20	3.0	4.21	3.54	4.05
17.	Break-Even Point	13.00%	34.50%	28.00%	44.00%	33.00%	33.60%	36.60%	43.50%
18.	Recurring F.E./Yr. Rs. Lakhs/yr.								
	(*i*) Raw Materials	1152.44	1047.00	1012.00	910.00	412.70	506.00	1160.00	796.00
	(*ii*) Maintenance material & spares	3.44	9.42	6.96	12.88	34.70	33.70	20.00	28.20
	(*iii*) Loan Repayment of F.E.	43.50	65.60	72.00	94.70	260.00	244.00	138.00	212.00
	Total, Rs. Lakhs/yr.	1199.38	1122.02	1090.96	1017.58	707.40	783.70	1318.00	1036.20

taking into account the cost of production, cost of distribution, and transportation, etc. The high returns on capital for first three schemes—imported ammonia and imported phosphoric acid—are due to very low investment as these are nothing but mixing plants only.

It has been shown earlier that on total plant nutrient basis, the cost of production of nitricphosphate is cheaper than that of DAP. In the ultimate analysis the costs of nitrogen and P_2O_5 in DAP would be dependent on those of rock phosphate, ammonia and sulphur and in nitricphosphate on those of rock phosphate and ammonia. Both the products contain nitrogen and P_2O_5 in different proportions. It would be interesting to investigate the cost of introducing these nutrients into the products and their relative costs in the products. This type of analysis will lead to a correct evaluation of these nutrients in a complex fertilizer.

As the two products contain nitrogen and P_2O_5 in different proportions and as both the nutrients are plant foods, for comparison it is simpler to keep the total nutrient in the two products same. In the following exercise this has been kept at 128,000 te/yr. of ($N+P_2O_5$). The corresponding capacity of DAP (18:46:0) and sulphate recycle nitricphosphate (25:16:0) of same water solubility are 2,00,000 and 3,12,000 te/yr. of products respectively. The Odda nitric phosphate and phosphonitric schemes are excluded due to their limitation in water-solubility of P_2O_5. In the sulphate recycle nitric phosphate the same degree of water-solubility as in DAP can be achieved and hence justifies the comparison between themselves.

In the nitric phosphate process, the nitric acid used for acidulation of the rock contributes in the introduction of $N+P_2O_5$, and so its cost will be shared by nitrogen and P_2O_5 on the basis of quantities present (40 per cent N+60 per cent P_2O_5) in the product[2].

The ammonia forms the ammonium compound, so its cost will go to nitrogen. Rock phosphate is the only source of P_2O_5 and hence its cost will be allocated to P_2O_5. The rest of the operating expenses like utilities, fuel, bags etc. and the fixed charges do not affect the nutrient content and are allocated between nitrogen and P_2O_5 proportionately.

In the case of DAP, the ammonia used for neutrali-

zation contributes nitrogen in the product. Hence, the cost of ammonia will be allocated to nitrogen. If the phosphoric acid used in DAP is imported, its cost as such is allocated to P_2O_5. And when the phosphoric acid is indigenously manufactured with imported rock and sulphur (for sulphuric acid, which is ultimately required for wet process phosphoric acid production), their costs also will be charged to P_2O_5 in DAP. The cost of utilities, labour and overheads, maintenance materials, bags and fixed charges are distributed over the total nutrient content in DAP.

The total investment of sulphate recycle nitric phosphate (25:16:0) and that of DAP (18-46:0) including the off-site facilities are presented in Table 3 and the raw materials and utilities consumption in Table 4. The

TABLE 3—Plant Investments for DAP and Nitric Phosphate Production Schemes

(Figures in Rs. Lakhs)

Sl. No.	Item	Plant Capacity, Te/day	DAP Scheme		Nitric Phosphate Scheme	
			F.C.	Total	F.C.	Total
1.	Erected Cost of Main Plants					
	(*a*) Sulphuric Acid	810	40.00	322.00	—	—
	(*b*) Phosphoric Acid	300	97.00	412.00	—	—
	(*c*) Diammonium Phosphate (18:46:0)	668	60.00	225.50	—	—
	(*d*) Nitric Acid	476	—	—	115.00	316.30
	(*e*) Liquor Ammonium Sulphate Plant	540	—	—	89.50	230.30
	(*f*) Nitric Phosphate (25:16:0)	1040	—	—	161.14	469.14
2.	Off-Site Facilities		22.00	236.00	60.00	582.00
3.	Contingency		10.95	59.25	21.28	79.89
4.	Initial Working Capital & Spares		231.20	281.38	76.00	181.02
5.	Financing Charges		—	53.76	—	65.60
6.	Total Investment		461.15	1,589.89	522.92	1,924.25
	(*i*) Total Nutrient Output ($N+P_2O_5$) te/yr		1,28,000		1,28,000	
	(*ii*) N, te/yr.		36,000		78,000	
	(*iii*) P_2O_5, te/yr.		92,000		50,000	
	(*iv*) Diammonium Phosphate Capacity, te/yr (18: 46:0)		2,00,000		—	
	(*v*) Nitric Phosphate capacity te/yr. (25:16:0)		—		3,12,000	

TABLE 4—Raw Materials and Utilities Consumption Per Tonne

Sl. No.	Item	Sulphuric Acid (100%)	Phosphoric Acid (P_2O_5)	DAP (18:46:0)	Nitric Acid 100% (Motor Driven)	Nitric-phosphate Complex (25:16:0)
1.	Raw Materials					
	(*a*) Ammonia, te	—	—	0.228	0.29	0.189
	(*b*) Sulphur, te	0.338	—	—	—	—
	(*c*) Rock Phosphate (32% P_2O_5), te	—	3.24	—	—	0.503
	(*d*) Gypsum (Make-up), te	—	—	—	—	0.128
2.	Utilities and Fuel					
	(*a*) Fuel Oil, Kg.	—	23.6	33.00	—	10.00
	(*b*) Power (KWh)	16.00	250.00	80.00	260.00	93.50
	(*c*) Cooling Water, m^3	12.34	15.00	6.00	13.80	5.70
	(*d*) Steam (L.P.), te	(−)0.75	0.884	0.02	(−)1.38	1.64
	(*e*) Process Water, m^3	—	—	—	—	3.44
	(*f*) Boiler feed water, m^3	—	—	—	1.40	0.61
3.	Intermediate Product					
	(*a*) Sulphuric Acid, te.	—	2.77	—	—	—
	(*b*) Phosphoric Acid (P_2O_5), te.	—	—	0.483	—	—
	(*c*) Nitric Acid, te.	—	—	—	—	0.503
4.	Catalyst	0.06 (Litre)	—	—	150 (mg)	—

total fund requirements (including financing charges, initial working capital and spare) of nitric phosphate plants is about 20 per cent higher than that of DAP.

In Fig. 1(a)*, the production costs of the P_2O_5 in nitric phosphate and DAP are plotted against ammonia and sulphur prices in Rs./te as variables respectively. It shows that at ammonia price of Rs. 300/te, the cost of P_2O_5 nutrient in nitric phosphate is Rs. 1210/te whereas at current sulphur price of Rs. 470/te, the cost of P_2O_5 nutrient in DAP works out to be Rs. 1450/te. The cost of P_2O_5 nutrient in DAP and nitric phosphate equalizes at ammonia and sulphur price of Rs. 130/te. each. In Fig. 1 (b)**, the cost of production of P_2O_5 in nitric phosphate and DAP are plotted against cost of ammonia and cost of phosphoric acid in Rs./te as variables. It shows that at present imported price of phosphoric acid at Rs. 1058/te of P_2O_5, the cost of P_2O_5 in DAP is Rs. 1347/te.

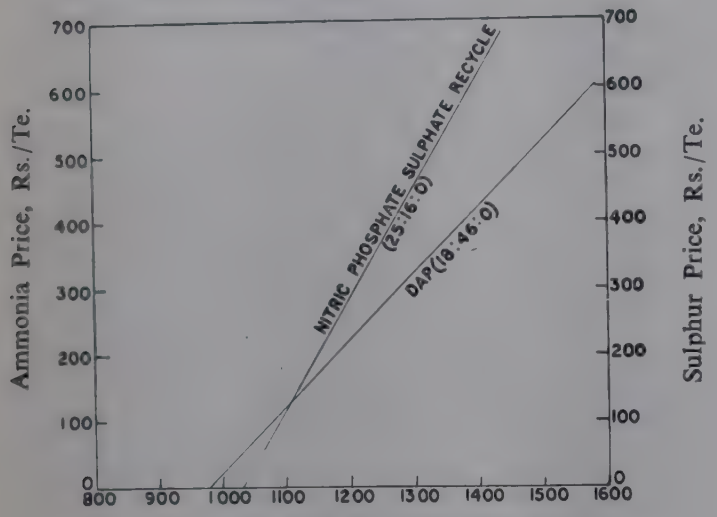

Fig. 1(a)—Cost of P_2O_5 Nutrient, Rs/Te

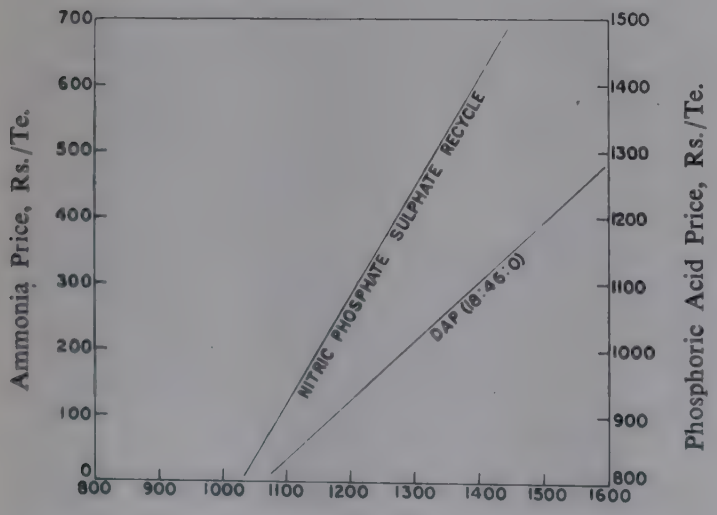

Fig. 1(b)—Cost of P_2O_5 Nutrient, Rs/Te

Fig. 2(a)* represents the cost of nitrogen nutrient in the product against the variable ammonia price. At Rs. 300/te, the costs of nitrogen work out as Rs. 705/te and Rs. 550/te in nitric phosphate and DAP respectively. The cost of nitrogen in the two products equalizes at ammonia price—for the case of indigenous phosphoric acid and ammonia bought from outside—of Rs. 820/te; below this, the cost of nitrogen nutrient in nitric phosphate is always higher than the same in DAP for a particular ammonia price. Fig. 2(b)** shows that cost of nitrogen nutrient of DAP is Rs. 590/te as compared to Rs. 705/te for nitric phosphate when the

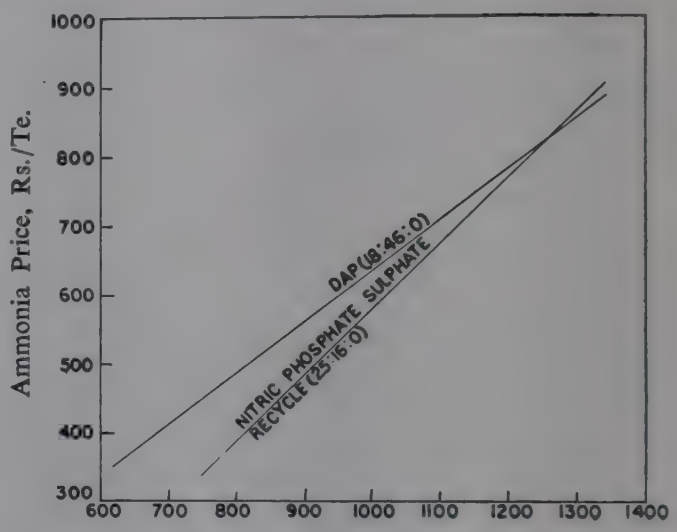

Fig. 2(a)—Cost of N Nutrient Rs/Te

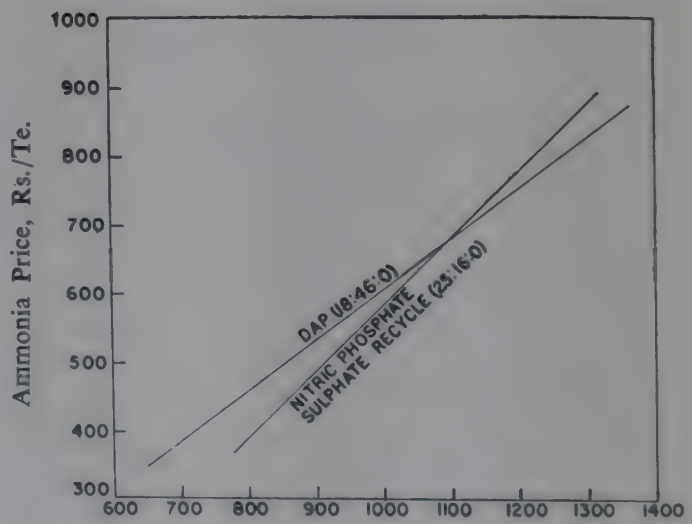

Fig. 2(b)—Cost of N Nutrient Rs/Te

*In the case of indigenous phosphoric acid and ammonia obtained from outside.

**In the case of both phosphoric acid and ammonia obtained from outside.

ammonia price is Rs. 300/te. The cost equalizes at ammonia price of Rs. 680/te, above which its cost in nitric phosphate is always lower than that in DAP.

To compare the viability of the two schemes it is logical to compare the returns on total capital employed. The profitability as per cent return on investment is gross profit after depreciation but before interest on borrowings and taxation, (i.e. sales realisation less works cost and depreciation) divided by the total capital employed.

In Fig. 3(a)* percentage return on total capital is plotted against sulphur price as variable and ammonia price as parameter for the case of DAP (manufactured with indigenous phosphoric acid) and for nitric phosphate case, returns are calculated corresponding different ammonia prices. From the graph it can be seen that at Rs. 300/te of ammonia cost, the percentage return on total capital is 28 for nitric phosphate. At the ammonia price of Rs. 300/te and sulphur price of Rs. 470/te, the corresponding return is 20 per cent for DAP.

In a similar manner for DAP production from imported phosphoric acid, the Fig. 3(b)** shows that with the existing price levels of phosphoric acid and ammonia at Rs. 1058/te P_2O_5 and Rs. 300/te respectively, the percentage return comes to 58. The higher return is due to lower investment (only DAP plant), at the expense of recurring foreign exchange for the import of intermediates.

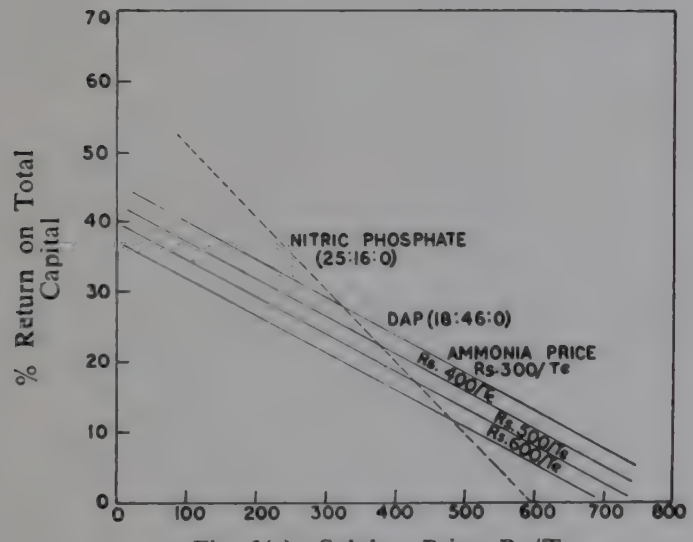

Fig. 3(a)—Sulphur Price, Rs/Te

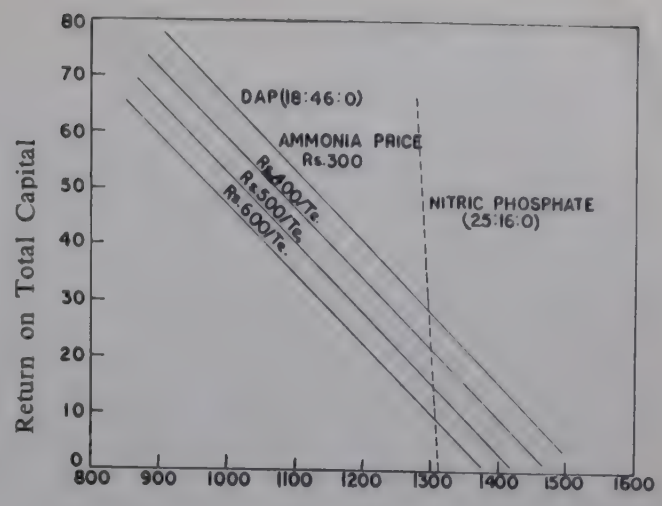

Fig. 3(b)—Phosphoric Acid Price, Rs/Te of P_2O_5

With the introduction of modern improved technology of single train larger capacity ammonia plant using centrifugal compressor on a steam-intensive process, low cost ammonia can be processed and subsequently the cost of production of nitric acid may be brought down considerably making the nitric acid route for nitric phosphate production attractive.

The economics projected above shows that nitric phosphate can compare favourably and compete successfully with DAP production, either with imported or indigenous phosphoric acid. Hence, there is no economic justification for the facile argument that phosphatic fertilizers produced from imported intermediates will be economical and cheaper to the producer, farmer and the country. The conclusion drawn from the above study is that the nitric phosphate route has immense potentiality in the present Indian condition.

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Rethinking on Special Relativity Theory*

By

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It has been argued here that in the special relativity theory the concept that the velocity of light is the highest which practically no material particle can attain is untenable and misconceived. Considering the mass associated with photon, it can be clearly seen that a particle can exist even at a velocity greater than c without attaining infinite mass.

In his communications[1–4], H. Dingle has presented logically convincing arguments against the Special Relativity Theory. His equations

$$\frac{\text{rate of A}}{\text{rate of B}} = \frac{t_1}{at_1} = \frac{1}{a} \quad > 1 \qquad (1)$$

$$\frac{\text{rate of A}}{\text{rate of B}} = \frac{at'_2}{t'_2} = a \quad < 1 \qquad (2)$$

show how under identical physical conditions a pair of clocks can record erroneous timings and also how their rate-ratios become self-contradictory.

Born's[5] as well as McCrea's[6] arguments against Dingle's findings are not to the point. McCrea's statement: "Using no more than Lorentz transformation in his algebra, he claims to derive two different values for the same quantity. But the transformation is linear and any result it gives can only be unique", reveals that McCrea believes, like most of the modern theoretical physicists, that one can reveal the laws of Nature by making use of complicated mathematics only. I do not know if he will agree with my comments that in present time most of the problems of physics have been confused by the complicated mathematical formulae and that there are increasing tendencies among the theoreticians to attribute in the first case, some imaginary property to Nature and then try to reveal on its basis other natural laws. This is one of the main reasons that the present-day theoretical physics is in a confused state. The most recent example of such state may be found in a paper on "Closures, Locality, and the Bootstrap" by Chew[7].

Whatever be the case, the fact is that Dingle, with sound logic, has obtained conflicting values for the same quantity and it must not be ignored. I present the following new case against the special relativity and hope this should convince McCrea that there is indeed something wrong with this theory and hence its very postulates on which it is based need rethinking and revision.

The famous mass-energy relations of Einstein is:

$$E = mc^2 \qquad (3)$$

Also from Planck's quantum theory

$$E = (n + \tfrac{1}{2})h\nu \qquad (4)$$

As Einstein himself showed the photons of average frequency ν must be associated with some mass, otherwise the photoelectric effect could not be explained.

Now, let us assume in both the cases, represented by equations (3) and (4), that exactly the same amount, say one gram, of the same matter is entirely converted into energy, at one time in accordance with (3) and at the other in the form of photonic emission as required by (4). Then energy emission in both the cases must be same; that is,

$$mc^2 = (n + \tfrac{1}{2})h\nu$$

$$\text{or} \quad n = \frac{2mc^2 - h\nu}{2h}$$

which is the number of photons in one gram of matter.

*Dedicated to इदं नमः ऋषिभ्यः पूर्वजेभ्यः पूर्वेभ्यः पथिकृद्भ्यः
To the seers of Mithila, our ancestors, the first path-finders.

Then clearly the mass of one photon is

$$\frac{m}{\frac{2mc^2-h\upsilon}{2h}}$$

$$= \frac{2mh\upsilon}{2mc^2} \qquad m = 1$$

$$= \triangle M \text{ (Say)}$$

$\triangle M$ must be very small yet it is a finite and non-zero mass. This is the mass of the photon at the velocity of light.

Now we calculate the relatively rest mass of the photon. The concept that the rest mass of the photon must be zero must be wrong. Because, in that case how a nothing (photon at rest) will become something ($\triangle M$) at high velocity. Thus, the concept: Something out of nothing is untenable[8,9]. Hence the photon at rest must be having some mass, although infinitely small yet finite.

In order to calculate the photonic rest mass say m, which must have, as we have argued, some finite positive mass let us consider the photonic mass at a velocity $v \simeq c$ but $v < c$. We can therefore safely conclude that there will not be any appreciable difference in the photonic mass at the two velocities v and c and so $m_v = \triangle M$ where m_v is the photonic mass at velocity v.

Then, from the relation

$$m_v = \frac{m_o}{\sqrt{1-\frac{v^2}{c^2}}}$$

we have

$$\triangle M = \frac{m_o}{\sqrt{1-f}} \text{ where } f = \frac{v^2}{c^2} < 1$$

because $v < c$

or $$M = \frac{m_o}{\sqrt{I}} \text{ where } I = (1-f) < 1$$

Hence $m_o = \triangle M \sqrt{I}$

The R.H.S. when substituted for $\triangle M$ will be extremely small quantity but nevertheless greater than zero.

Now, if the special relativity theory is correct, according to which any finite mass at the velocity of light must become infinite, it becomes erroneous because from the calculations made above it is clear that the exceedingly small yet finite photonic mass, $mo = \triangle M \sqrt{I}$ remains only finite even at the velocity of light which must not have been so if the theory were correct. Hence, something is wrong with the very postulates of the theory and we must, therefore, revise them and give rethinking to the theory's findings.

The same conclusions can be arrived at by using de Broglie's famous relation $\lambda = \frac{h}{mv}$ where m may be considered the mass of the photon.

It is interesting to note that Dicke[10] has also come to the conclusions that in the initial period of universal expansion from the Primeval Fire Ball the Universe expanded at a velocity several thousand times greater than the velocity of light c. Also, Sudarshan[11] and others have shown mathematically that particle called tachyons can exist at a velocity $> c$ and that there should be nothing like a light barrier.

Acknowledgements

I am grateful to my brothers, Dr. Chandra Shekhar Mishra, D.Sc. (Engg.) of Bokaro Steel Ltd., for encouragement and Sri Shashi Shekhar Mishra of Allahabad University for criticisms. My sincere thanks are due to Sri S. N. Roye, our Editor, for changing the original title—Why the Special Relativity Theory is Erroneous—to the more appropriate, present one.

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Editor's Note: This Letter was sent to Prof. Herbert Dingle, FRS, of England for comments. Below are his observations: *'I think the author's conclusion concerning the finite mass of a photon at rest is correct, but it could have been reached more simply from the experimental fact that light exerts a finite pressure, and therefore photons possess a finite mass, m_v. Since a perfect vacuum is unattainable, the velocity of light in these experiments was less than c, and therefore according to the special relativity equation, $m_o = m_v\sqrt{1-v^2/c^2}$, m_o is the product of two finite quantities, and cannot be zero. Hence, the mass of a photon, and therefore the pressure of light, should increase indefinitely as the pressure is lowered in the experimental chamber'.*

Technical Digests

Import Substitution in Fertilizer Industry

Import substitution came into a sharp focus during the last emergency which resulted in the Get-Together of Research and Industry in December 1965 organized by the CSIR at New Delhi. It is an exercise in self-reliance and an assertion of determination to stand on one's own feet. Not only the imported goods but even the know-how, which is sought from the developed countries at present to fill the gaps in our technical expertise, has got to be replaced progressively by our research and developmental efforts. To take stock of the present position and also realising the paramount need for a faster development of the chemicals and fertilizers industry during the Fourth plan and reducing the quantum of avoidable imports, the Indian Chemical Manufacturers Association organized a seminar on the theme of the complementary roles of (i) research and development and (ii) industry in import substitution. In a paper* presented at the above seminar, the role of the Planning and Development Division of FCI Ltd., in the substitution of imported technical know-how be developing indigenous ones and in attaining self-sufficiency in fertilizer production, has been highlighted.

FCI had been aware as early as 1951, when the Sindri factory was put on stream on a turn-key basis, that in fertilizer and chemical industries the pace of technological innovation is very rapid. It was also realised that unless the country builds up its own technological know-how, the package deals with foreign concerns, like the one mentioned above, are going to be perpetuated. However, for achieving self-reliance the various disciplines, which contribute to fertilizer technology, shall have to be harnessed together in an integrated manner. The various functions involved are technological and basic research, development, planning, technoeconomic feasibility studies, process technology, design, engineering, fabrication construction and installation, etc. The efforts of the division, which came into existence in 1961, have led to the substantial reduction in the foreign exchange components of several of the FCI's projects, viz. Durgapur and Barauni, in comparison to its earlier projects viz. Nangal, Trombay, etc. (Table 1); the comparatively high figure in the case of Namrup being mainly because of the smaller plant sizes. The degree of participation in the execution of these projects has also progressively increased from a meagre portion in the case of Nangal to a very large extent in

TABLE 1—Capital Requirements and Capacities of Fertilizer Projects under FCI Ltd.

Sl. No.	Units	Year of Completion	Total Nutrient, 1000 te	Total Project Cost, Rs. lakhs	Foreign Exchange, Rs. lakhs	Foreign Exchange, $/te. yr. Nutrient
1.	Nangal	1959	80	3120	1426*	374
2.	Trombay	1965	125 (including P_2O_5 also)	4156	2035	300
3.	Gorakhpur	1967	80	3316	1438	240
4.	Namrup	1968	45	2320	671*	368
5.	Durgapur	1970	152	4363	1448	127
6.	Namrup Expansion	1971	152	3760	1380	121
7.	Barauni	1971	152	4500	1370	120

(*=Pre-devaluation figure)

*'Import Substitution in Fertilizer and Chemical Industry: Role of P & D Division of FCI Ltd.,' Paper presented at the Import Substitution Seminar held under the aegis of ICMA at Calcutta during Aug. 29-30, 1968.

Barauni. The foreign exchange component per tonne-year of nutrient of the latest projects viz. Durgapur, Namrup Expansion and Barauni—for whose design, engineering and commissioning FCI is responsible—is also much low.

On an average, the foreign exchange saved comes to about $ 40/te year (or Rs. 300/te year). So for a plant of 1,50,000 te of nutrient the foreign exchange saving would be about Rs. 4.50 crores. Considering the number of plants required to meet the 4th Plan target a saving of about Rs. 50 crores would be effected. The potential savings in foreign exchange on account of progressive indigenization in process know-how, design and engineering, catalyst development, etc. are given in Table 2.

TABLE 2—DETAILS OF FOREIGN EXCHANGE SAVINGS

(Rs. in lakhs)

Sl. No.	Items	To date	Potential Upto 1973-74
1.	*Products manufactured but not available indigenously:*		
	(*a*) Catalyst	160	1,000
	(*b*) Chemicals	30	345
	Sub Total (1)	190	1,345
2.	*General and Intensive Planning:*		
	(*a*) State and districtwise assessment of fertilizer requirement for the 4th Plan	7	7
	(*b*) Criteria for the choice of nitrogenous & phosphatic fertilizers in India	11	—
	(*c*) Techno-economic feasibility reports and other reports for various projects	112	23
	(*d*) General Consultancy Services	22	20
	Sub Total (2)	152	50
3.	*Design, engineering and procurement*	1,165	2,218
4.	*Indigenisation of equipments*	142	400
5.	*License fees and Royalties due* to Know-how developed by P & D Division*		
	(*a*) Gasification Processes	90	450
	(*b*) Purification Processes	5	200
	(*c*) Sulphuric acid, nitric acid & phosphoric acid processes	18	89
	(*d*) Am. sulphate, cal. ammonium nitrate, nitrophosphate and TSP plants	13	84
	Sub Total (5)	126	823
	GRAND TOTAL (1+2+3+4+5)	1,775	4,836

*Besides these there are even other process know-hows developed by P & D Div., the utilisation of which holds a potential asset if and when used by the chemical industry.

The development of indigenous know-how and facilities for catalyst production is an important contribution of this division which not only helped to maintain the country's fertilizer production without depending on foreign exchange but has also given confidence and impetus to meet the requirements of most of the catalysts used in fertilizer industry. Its gas reformation catalyst is being used by the Sindri Unit for the last several years. Another catalyst, viz. for steam reformation of naphtha and natural gas, has been perfected to such a degree that the Barauni and Namrup fertilizer expansion reformation plants are being designed on its basis. The savings in royalties on the score of the last catalyst on the basis of the total capacity of fertilizer plants (say, about 1.5 million tonnes of N), using naphtha reformation, that are coming up during the next 2 or 3 years, will be of the order of Rs. 450 lakhs provided this Division is allowed to design the reformer based on this developed know-how. In fact, this Division is one of the very few organizations in the world possessing its own catalyst know-how.

P & D Division is capable of taking up assignments covering the complete process know-how, detailed engineering, procurement, erection and commissioning in the field of fertilizer and related heavy chemical industries. It has developed pilot plant facilities for studying new processes to collect data for executing commercial plants based on them. The design and engineering of the entire ammonia plant beginning with desulphruization to ammonia synthesis and urea production have been taken up by this Division.

It has already supplied plants for production of nitric acid, mixed fertilizers and for storage and handling of liquid ammonia. On the score of its design engineering and procurement activities, it has saved about Rs. 1,165 lakhs. It has remained the constant endeavour of this Division to reduce the foreign exchange component of the projects by using more of indigenously available equipment, machinery and facilities of fabrication. It may be incidentally mentioned here that the hortonsphere for storing liquid ammonia and scraper used inside fertilizer storage silos will henceforth be fabricated within the country based on design and engineering done by this division. Such efforts of indigenisation of equipment have yielded savings to the tune of Rs. 142 lakhs.

On the basis of process know-hows developed at this division as part of our product developmental efforts, some of the chemicals, such as ammonium bicarbonate, cation-exchange resin, polyphosphate, silica gel, sodium nitrite and nitrate, have been or are going to be put

on a commercial scale at Sindri and Trombay, etc. This would also effect a foreign exchange saving to the tune of Rs. 30 lakhs so far.

In addition to acquiring know-hows of certain well-known processes from reputed foreign parties, like Montecatini-Edison of Italy in regard to ammonia and urea syntheses, P & D Division has developed its own design and engineering know-hows. Its first venture was the design of the 820 te/day nitric acid and 2000 te/day CAN** plants at Rourkela which are in operation for the last several years. The design and engineering of the steam-reformation in respect of the Durgapur fertilizer project, for which FEDO'S*** services were requisitioned, is now being undertaken by this Division, employing its own catalysts, which will also be used in the future projects, like Barauni. In all such efforts, the emphasis has been on the use of indigenous raw materials and equipment, some typical examples of which are (i) the development of sulphuric acid manufacture from natural or by-product gypsum and (ii) recommendation of nitric phosphates instead of sulphur-based phosphatic fertilizers. Some of these processes have been covered by our patents and the foreign exchange savings effected are of the order of Rs. 126 lakhs.

It has been felt that the existing facilities in the engineering industry in the country are not sufficient to meet the requirements of the fertilizer and chemical industries, such as design and manufacture of high pressure vessels, heat exchangers and waste heat boilers, compressors (of the order of 200 HP), manufacture of S.S. pumps and multi-stage centrifugal and reciprocating pumps, heat exchanger tubes, SS valves, and carbon steel and alloy steel valves of over 1000 Kg/cm^2 pressure and the design of furnaces. Moreover, there is considerable reluctance or lack of initiative on the part of Indian manufacturers to cater to the requirements of forged flanges and fittings or carry out procedure tests and develop satisfactory methods for fabrication.

It may also be worthwhile mentioning here that some of the present policies are not in tune with indigenization and import substitution, such as import of liquid ammonia and phosphoric acid, which will impair the growth of engineering industry.

Some of the know-hows developed/acquired by this division are enumerated as follows: A. *Developed:* 1. Gasification—(i) semi-water gasification and slagging gas generator (ii) primary and secondary steam reformers (iii) synthesis gas manufacture from naphtha; 2. Sulphur removal—desulphurization of (i) synthesis gas by iron oxide, (ii) hydrocarbon vapours by iron oxide/alkalised iron mass (iii) carbon dioxide used for urea manufacture—by zinc solution and (iv) hydrocarbons; 3. Shift conversion at various pressures and at high or low temperatures; 4. Purification of synthesis gas by removal of CO and CO_2 by (i) Copper liquor and caustic soda at high pressure and (ii) Methanation; 5. Refrigeration of synthesis gas and storage of ammonia; 6. Nitric acid plant including vaporization, oxidation and absorption at medium pressure. 7. Complete units of calcium ammonium nitrate, ammonium nitrate and double salt. 8. Manufacture of ammonium sulphate by (i) neutralization of ammonia with sulphuric acid or using natural or by-product gypsum. 9. Manufacture of phosphatic fertilizers, viz. triple superphosphate, ammonium phosphate, nitrite phosphates with different amounts of water-soluble P_2O_5; 10. Mixing plants for complex fertilizers; 11. Catalysts—Desulphurized iron oxide mass, alkalized iron catalysts, active carbon, desulphurization catalyst, low and high temperature shift conversion catalysts, reformation and methanation catalysts, ammonia synthesis catalyst (its manufacture will start in early 1969); 12. Design and engineering of water and effluent treatment plants, process technology, design and engineering of ion-exchange resins for water treatment; 13. Design, engineering and manufacture of ammonium bicarbonate plant; 14. Process know-how, design and nitrous gases; 15. Sodium polyphosphate using indigenous materials. 16. Recovery of carbon from Shell's partial-oxidation gasification process; 17. Silica gel, etc.

B. *Acquired:* 1. Complete know-how for design and engineering of large scale ammonia and urea plants. 2. Complete know-how for design and engineering of large-scale manufacture of sulphuric acid from pyrites from M/s. Techno Export of Bulgaria. 3. Process know-how for CO-removal from synthesis gases based on Giamarco Vetrocoke process.

Carbon Black from Waste Slurry of Petroleum Oil Gasification*

During gasification of petroleum oils finely divided carbon is formed, which during washing forms a slurry—containing about 2 g. of carbon/100 ml.—creating a disposal problem. About 0.3-0.5 ton of carbon is, thus, produced from one ton of petroleum feedstock. In some works, this carbon is converted into pellets which are then burnt in boilers.

**Calcium ammonium nitrate.

***The design organization of the Fertilizers & Chemicals Travancore Ltd. (FACT), Udyogamandal, Alwaye (Kerala).

A process has been developed in this laboratory* for preparation of carbon black from this slurry. Carbon is separated by pelletting with a petroleum oil, most of the latter being recovered during the heating of the pellets and condensation of the vapours. The product is of high purity containing less than 0.1 per cent ash; it is extremely fine and is suitable for use in paints, printing ink, rubber industry, etc.

The process consists of (i) agitating the carbon slurry with petroleum oils till the former is separated in the form of pellets (ii) separation of the carbon pellets from the water and heating them to form carbons black. The carbon pellets are separated by draining the mixture of pellets and water through a wire screen. The pellets can then be heated by direct or indirect steam, hot gases or indirect fire. The petroleum oil may be gasoline, diesel oil, kerosene, gas oils, furnace oils or mixtures of these oils.

*A process for the preparation of carbon black from carbon slurry produced during gasification of petroleum oils (Inventors: M. M. Mazumdar, B. K. Dutta & K. R. Chakravorty, P & D Divn., FCI Ltd., Indian Pat. No. 103573 E).

Notes & News

Seminar on Coal and Coal Chemicals at Sindri

A seminar on coal and coal chemicals, organized under the joint auspices of the Calcutta Regional Centre of the Indian Institute of Chemical Engineers and the Coke Oven Managers' Association (Indian Branch), was held at Sindri during November 2-3, 1968 with FCI Ltd., playing the host and Sri Suku Sen, a former General Manager of Bhilai Steel Plant and a well recognized steel technologist, presiding. Sri Ranchod Prasad, Chairman, National Coal Development Corporation, who was the chief guest, in his inaugural speech highlighted the importance of coal in the national economy of this country. The seminar was divided into the following 3 sessions: (i) Coal carbonization and by-product (ii) Coal as raw material for fertilizer and chemical industry and (iii) Chemicals from coal and by-products.

Session 1: At the first session, which was chaired by Sri Raju, Manager Coal Washery Plant Hindustan Steel Ltd., Durgapur, 14 papers were presented. In a paper, entitled 'Manufacture of Coal Washeries and Equipment in India,' Sri P. S. Prabhu (Dorr-Oliver Ltd.) reviewed the present facilities available in India for the design and construction of coal washeries. There are at present the following 13 washeries —mostly based on foreign process and following various flowsheets—under operation or under advanced stage of construction: Dudga I and II (each having capacity of 2.4m. tons/yr), Bhojudih (2.4), Patherdih (2.0), Durgapur Steelworks (1.5), Kathara (3.0), Gidi (2.84), Sawang (0.75), Kargali (2.72), Durgapur (W. Bengal Govt., 1.35), W. Bokaro (TISCO, 3.0), Jamadoba (1.6) and Chasnala (IISCO, 2.70). According to the original plan, about a dozen more washeries were to be put up by the NCDC by 1970-71. The equipments are of various origin, viz. British, American, Russian, German, Japanese, French, Polish and Czech, etc. With the implementation of projects like HEC (Ranchi), HEL (Bhopal), MAMC (Durgapur) and others, both in the public and private sectors, the stage has come where about 80 to 90 per cent of the coal washing equipment can be manufactured from indigenous sources. In drawing up plans and specifications for scrutinizing global tenders and conducting guarantee tests etc., the role of the Central Fuel Research Institute Dhanbad is noteworthy. The author highlighted the following problems for achieving self-sufficiency in putting up turn-key coal washeries: (i) Raw Materials: Shortage of alloy steel—to be supplied by Mysore Iron & Steel Co., Durgapur Alloy Steelworks and several other projects licensed in the private sector—is still a major problem which will continue for some more years. While the position regarding structural steel fabrication is satisfactory, the demand for steel plates of thickness 38-63 mm. is still a problem. The availability of heavy castings is also a problem and most of it is still imported as Heavy Engineering Corporation (Ranchi) quotes long delivery dates, (ii) Specialized Equipment and Auxilaries: Centrifuges, automatic samplers, magnetic separators, pulleys and special pumps have still to be imported as their manufacture because of inadequate demand is not worthwhile, (iii) Engineering Services & Process Know-how: As regards process know-how, the Central Fuel Research Institute has excellent pilot plant and bench-scale laboratories for executing complete projects and carrying out all kinds of washability investigations. In addition, project engineering and consulting services are now progressively available within the country itself who can design coal washeries and supply integrated plants on turnkey basis. Except some large castings, most of the crushing and grinding equipments are now available. Most of the material handling and fines recovery equipments are now manufactured within the country. While high HP motors are available from Heavy Electricals Ltd. (Bhopal), their delivery dates are very late; there is a large gap in the availability of variable speed drives and high HP reduction gears, etc. and complicated controlling instruments are still to be imported.

B. Banerjee, G. G. Sarkar and A. Lahiri (CFRI), have studied[1] the range of variation in the cleaning possibilities of the Jharia coals both in the vertical sequence and in lateral extents. The major *Barakar* measure coals show well-defined sequence in cleaning possibilities both from the point of view of regional as well as vertical distribution of the seams. In the vertical distribution following the stratigraphic sequence, two groups of seams are classified; the one comprising the upper horizon seams (XIII to XVIII) show better cleaning characteristics than the second group in which seams V to XII are included. In the regional distribution three regions or zones, viz. western, central and eastern, are marked out on the basis of the differences in the cleaning characteristics of the seams in the three zones. The coals in the western zone are poor, while those in the eastern and central zones show superior and medium cleaning characteristics. The coals deteriorate in cleaning potentialities progressively in the western direction. The tendency of the coals towards the west to have higher ash indicates that the quantum of mineral matter carried out during *drift* must have been much more in the western sector. The *Barakar* sediments thus show that the coarse-grained sandstones are more prevalent in the western part than in the eastern, which indicate that the above sediments in Jharia coalfield came from the west, causing settling of the heavier materials in the western parts and the lighter materials moving eastwards. *Barakars* diminish in thickness towards the east, while in the western part the seams are often split and interbanded.

The classification of these coals into three regions with well-defined horizons for each on the basis of their washability characteristics gives an instantaneous picture of the cleaning possibilities of these available in different areas. This classification may also serve as a guideline for selecting areas from which coals of required cleaning characteristics can often be drawn to suit to the designed specification of different central washeries and receiving their supplies from the different seams.

The characteristics of coke required for

[1] Regional Classification of Jharia Coals based on their Washability characteristics.

semi-water gas generation has not been well-defined in this country because except the Sindri fertilizers no other factory has adopted this process. M. Chandra, S. C. Biswas and B. K. Dutta (P. and D. Divn., FCI Ltd.) have enumerated[2] the following characteristics of coke for manufacture of such gas: (i) Ash Fusion characteristics: for maximum gas production and better carbon efficiency, the ash in the coke should soften just sufficiently so that coke reaction is enhanced and clinkers of small sizes are formed without complete fusion of any ash. The optimum ash fusion point should be such that smaller clinkers formed on the grate can be easily directed to flow to the ash boxes. For optimum operation, the softening point of coke ash in mild reducing atmosphere should be 1325-1400°C. (ii) Ash composition: Addition of lime, magnesia, alkali oxides and ferric oxide lowers the softening temperature of ashes whereas alumina raises it, based on which a method has been developed for predicting the softening temperature of coal ash in an oxidizing as well as mild reducing atmosphere from their chemical composition. This method has been used in the blending of coals in Sindri's coke ovens, (iii) Reactivity: High reactivity is conducive for greater steam decomposition which in turn results in more gas production. Optimum reactivity of coke towards carbon dioxide for gas generator has been found to range within 100-120, (iv) Strength of coke: coke should be strong enough to withstand mechanical shock and abrasion; usually 85 per cent on ½ in. screen satisfies hardness and in regard to abrasion resistance 75 per cent Micum 40 and 15 per cent Micum 10 indicate satisfactory strength, (v) Size: coke should have the following sizes—3 to 2 in. 5 per cent, 2 to 1 in. 80 per cent, 1 to 1/8 in. 10 per cent and −½ in. 5 per cent, (vi) Porosity: porosity of 40 per cent is optimum for coke, (vii) Ash content: 22-23 per cent ash in coke is desirable although higher ash coke has also been charged in the gas generators; moisture should be within 5 per cent.

Unlike in a steelworks, the coke ovens at Sindri are required to produce a coke suitable for gas generation and sufficient quantities of gas for processing into ammonia. The medium volatile coking coals of Jharia and weakly coking high volatile Raniganj coals have been studied by the authors in bench scale as well in box tests and also in plant scale in order to obtain a suitable blend. It has been found that a blend containing 40-50 per cent Jharia and 50-55 per cent Raniganj (Methani and Bhojudih) coals is quite satisfactory.

In their paper[3] A. C. Srivastava and B. K. Dutta (P & D Divn., FCI Ltd.) have shown that the cation-exchanger (named Sindex C 26), developed in this laboratory from coke oven waste products and which is cheaper than polystyrene and acrylic resins, can absorb from coke oven liquor ammonia, which can be reclaimed with 20 per cent sulphuric acid yielding a 14 per cent ammonium sulphate solution. The overall ammonia recovery is about 100 per cent and the acid consumption is about 2 per cent higher than the theoretical value required for neutralization. This compares very favourably with the conventional ammonia recovery processes where the recovery is never more than 99 per cent; moreover, there are several other advantages, viz. steam requirement is considerably less, since the process operates in cold corrosion and maintenance problems are less, effluent disposal is less troublesome, the finished product is of a better quality, operating costs and capital investment are less, etc.

V. P. Mittal (H.S.Ltd., Bhilai) discussed[4] the problem of maintenance in a by-product coke plant for maintaining high and continuous productivity at a minimum cost. A by-products coke oven plant comprises a coal handling plant, battery and coke sorting and by-product units. The main problems in the coal handling, apart from wear and tear on chutes of the conveyor section, are the hammers for the coal blend crushing and separation of any tramp iron from the incoming coal. The chute when lined with rolled manganese steel plates gives satisfactory results. Regular cleaning of the doors and door frames by the operational personnel can minimize to a great extent the problem of gas leakage and door burning.

The maximum problems are faced in the by-products plants where different equipments e.g. pumps, compressors, blowers, centrifuges, etc., handle very corrosive materials. Frequent leakage through glands has to be taken care of. Similar attention is needed for electric detarrer and sulphuric acid plant, and modification of parts and accessories suiting local conditions have to be effected.

Blast furnace technique will continue to reign supreme for many more years as the main technique of iron-making, so every effort should be made to reduce the coke rate in view of the dwindling resources of coking coal and mounting cost of coke. Although the captive coke oven plants find a ready disposal of their products in their own blast furnaces, the need for utmost economy in the production of coke and for an improvement in its overall quality is called for. N. N. Das Gupta (Carl Still Export GmbH) gave an outline[5] of some of the possible means of achieving the above objectives.

An obvious means of saving on both capital and operational costs is to go for large-size ovens. While in Japan two 6.5 m. high are already in operation his own firm is aiming in the near future to build 8 m. high ovens, whereas till lately the standard size was 4 m. Mechanization and automation to the extent essentially needed should be introduced to facilitate effiicient working. Among other measures suggested for adoption to minimize the cost of conversion of coal to coke are the following: strict adherence to efficient operational and maintenance procedures, predrying of the coals before charging, improvement in blending and coking practices, such as use of ovens of narrower width operated at the highest possible flue temperature, altered technique in the operation of blast furnace as in the Western USA, use of alternative fuels for under-firing of recovery and processing of by-products, introduction of some sort of interfirm comparison study to assess the relative efficiency and profitability of different plants.

With the possibility of getting the metallurgical coke-making industry localized in the present coal-steel belt of W. Bengal, Bihar, Orissa and M.P., and keeping in mind the fast dwindling coking coal reserves, S. N. Wazir (Design Bureau, H.S. Ltd., Ranchi) suggested[6] the following in respect of projecting and designing coke ovens: (i) ovens be constructed on piled foundation in order to cater for heat effect

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[2] Preparation of Coke at Sindri for Manufacture of Semi-Water Gas.

[3] Ammonia Recovery from Coke Oven Industries by on Ion-Exchange Process.

[4] Problem of Maintenance in a by-product Coking Industry.

[5] Some Random Thoughts on Our Coking Industry.

[6] Consideration for Design and Planning of Coke Plants in India.

on settlement; (ii) cooling towers and refrigeration plants should form part of coke plant while coal washery and power plant should not; (iii) coal handling and preparation operation be mechanized, incorporated with automatic rotary tippler and sampling facilities; (iv) finer and selective crushing should be resorted in conjunction with blending; (v) indigenous coke oven brick work design be developed; (vi) the limiting specifications and dimensions of important plant and equipment should be standardized to suit the Indian conditions, viz. ovens would be suitable having 400 mm. width with taper about 70 mm., 6 m. height and 17 m. length and underjet, compound air-pin turn flue ovens for combination heating improved design of bucstays, doors, flash plates accession pipes and single side hydraulic mains with waste heat channels.

In all large-scale coke oven plants, the disposal of the large volumes of toxic effluents is a serious problem. These are obtained from (i) plant leakages and washings comprising oils and tarry matter in suspension, (ii) benzol purification plant comprising acid sludge containing sulphuric acid and complex organic matter, (iii) ammonia still containing phenols, thiocyanates and thiosulphates, etc., (iv) ammonia sulphate saturators containing cyanides, sulphides, etc. The phenolic liquors being the largest in volume and most objectionable require special attention for disposal. R. R. Prasad and B. K. Dutta[7] (P & D Divn., FCI Ltd.) have cited the different methods of treatment of phenolic wastes, which can be divided into 2 groups—one for recovery and other for destruction of phenols.

In the biological oxidation processes for treatment of ammonia liquor, as practised at the Durgapur steelworks and IISCO Burnpur, besides the imported know-how, even the seed culture for oxidation is imported. The authors have developed in their laboratory an active culture from garden soil which requires much less time for oxidation of phenol. They have studied its activity with regard to the effects of temperature, pH and air rate which has shown that phenol up to 1170 mg./1. could be destroyed. A continuous pilot plant study has shown that phenol upto 440 mg./1. is destroyed completely in 6-7 hours at room temperature (29-34°C) and air rate $3M^3$/min./M^3 of liquor. For establishing the indigenous know-how on a firm ground, a commercial plant is being designed by them to treat $15M^3$/hr of wastes containing 400-600 mg./1. phenol.

The disposal of the highly corrosive and viscous coke oven acid sludge wastes is a problem. V. K. Seth[8] et al (P & D Divn., FCI Ltd.), have developed cation-exchanger resins (named as Sindex C 26 and CH-20) from this sludge and studied their various characteristics applications. The process consists of polymerization and sulphonation of the waste product under controlled digestion and crushing, washing and regenerating to produce an exchanger of the desired characteristics. C-26 is having an higher exchange capacity, moderate swelling and suitable exchange characteristics for water purification, whereas CH-20 has stability even at high temperature and under highly alkaline conditions. Both the products are hard, granular and capable of exchanging cation, infinite number of times, in solution. With proper regeneration, CH-20 has been found specially suitable for economic treatment of medium pressure boiler feed waters by using it in conjunction with hot lime softeners.

C-26 resin is useful in all water treatment processes operating either in hydrogen cycle for removal of cations or in sodium cycle in base-exchange softeners for removal of hardness of water. It can be used in a 2- or 3-bed or even in mixed-bed plants in conjunction with anion-exchangers. In a mixed bed with a strong base anion-exchanger, conductivity of the order of 0.1 micromhos/cm. can be easily achieved. It can be used in the recovery of copper from effluents, zinc from rayon wastes, heavy metals from planting wastes, etc. In the Sindri fertilizers factory both of the exchange resins are being produced commercially which is saving foreign exchange to the tune of Rs. 26 lakhs per year.

With the increasing emphasis on the development of organic chemical industry during 4th plan, coal chemicals are bound to play a very important role. While the potential of these chemicals is as below, tar 420,480; ammonium sulphate 154,000; light crude benzol 126,000; benzene 88,300; toluene 13,900; xylene 2500; solvents 3800; naphthalene 16,800; anthracene 8400; phenol 3400; pitch 227,000; creosote oil 84,000; and pyridine 1,600. the actual production (ton/yr.) is much less.

The economics of coal chemicals industry depends on (i) maximizing the recovery of primary by-products like tar, ammonia and light crude oil (ii) diversifying the chemicals produced and improvement in their quality and reduction in the cost of production of the individual items. With progressive deterioration in the quality of coal the yield of the by-products decreases. Besides improving the technology of blending, changes like keeping the gas temperature after gas coolers as low as possible for improving the yield of tar and use of chilled water for maintaining the temperature in the crude benzol plant, etc. can be effected. By catalytic hydrogenation of crude benzol under pressure an high yield of pure benzol is obtained.

So far, coal chemicals industry was concerned mainly with the recovery of the primary by-products, viz. tar, ammonia and crude benzol, and their further processing for obtaining a few chemicals, but now with the development of pharmaceutical, dyestuff and other industries, there is a potential demand for pyridine, pitch as a binder and anthracene and the demand for cyclo-pentadiene, carbazole, coumarone, indene, acenaphthene, carbazole and fluorene, etc. is also picking up. However, the increase in the price of coal is inescapable and has to be largely counteracted by strict control on the cost of production of the individual chemicals and on the consumption of energy.

In a paper* entitled 'Integrated Coke Plants for Economy', read by one of its authors, S. Ranga Raja Rao (CFRI), at a later session, the several of the integrated coal processing complexes originally planned and proposed by the Central Fuel Research Institute have been discussed. Most of coalfields are situated in the peninsular India and Assam, which are well served by river basins. The integration proposed were (i) after beneficiating high ash coking coal the cleans can be utilized in metallurgical industries while the inferior grades, rejects, middlings etc. utilized *in situ* or near the washeries for power generation; (ii) to integrate the use of coal—coking or non-coking—with production of iron and steel and utilize the surplus coke oven gas either for fertilizers and chemicals manufacture or for transmission to urban areas by gas grids for domestic use, and the by-products, viz. tar and benzol, can be treated for manufacture of chemi-

[7] Coke Oven Effluents and their Treatment.

[8] Utilization of Waste Acid Sludge of Coke Oven Plant For production of Cation-Exchange Resin.

* by S. K. Sen., S. R. R. Rao & A. Lahiri (CFRI)

cals; (iii) to produce a smokeless fuel by low or medium temperature carbonization of non-coking coal, integrated with pig iron manufacture in a low-shaft furnace and the gas, where surplus, is converted to fertilizers or chemicals and tar and benzol processed to chemicals. For the inferior coals, not amenable for carbonization, fluid carbonization can be adopted producing tar, gas and powdered char, which can in turn be briquetted and used for metallurgical purpose.

In all the integrated schemes the ultimate aim is to produce high grade coke at an optimum cost, which in turn is dependent on the capital cost of the plant and cost of raw materials. Where the coke plant is not integrated with a steelworks, the cost of coke may be more if the by-products are not processed; but such a venture can be profitable if the entire liquid and gaseous by-products are fully processed and utilized. For production of a domestic industrial fuel by low or medium carbonization of non-coking coal, it is essential that an independent assessment be made of its economic viability, for which the costing of the two parts viz. coke making and by-products processing has to be dealt with separately.

The authors have discussed the pattern of integration in the following complex/ projects: Ramgarh, Durgapur coke ovens and Talcher. About Ramgarh, three possibilities based on the large coking coal deposits between Ramgarh and Bokaro steel plant have been conceived depending upon capital investment, viz. minimum integration involving Rs. 60 crores, 'partial integration' (Rs. 70 crores) and full integration (Rs. 80 crores). The basic scheme is to carbonize 400 t/d of a blend of Ramgarh and Jharia coals to produce foundry coke, small coke (80-13 mm.) for utilization in low shaft pig iron furnace and the surplus coke oven gas for making ammonia and urea.

The Talcher complex, based on the utilization of non-coking coals in the area, is envisaged to consist of a retort carbonization plant (coal throughput 1600 t/day), wherefrom the sized coke will be used for production of 520 t/day pig iron from low shaft furnaces and the surplus gas to be used for ammonia and finally urea production. Two capacities, viz. 250 and 420 t/day, of urea plant have been proposed. The total capital estimated is Rs. 30.7 and Rs. 35 crores respectively.

W. Hilgert and N. N. Das Gupta (Carl Still) described[9] a travelling grate stoker carbonization process (patented by CFRI, Indian patent no. 61020) based on which a plant has been built by their firm at Hyderabad in 1966 for manufacture of coke for domestic and industrial use. The process can use all types of coal—from non-coking to coking—upto 100 mm. size and can be built of any capacity to suit local conditions. Both in capital and operational costs such plants will be cheaper. Other advantages are: high flexibility in regard to the type of coke or char produced, easy to start and operate and possibility to interrupt, less stringent requirement of refractories, low maintenance cost, quick replacement of damaged parts, the reaction gases can be utilized for various industrial purposes, etc.

The coke produced in the Hyderabad plant—which consists of 2 travelling grate stokers of about $2m^2$ area each and has a carbonization capacity of about 20-25 tons/day of coal—has been tested in a domestic 'chullah' and found absolutely smokeless. The time for the ignition of the coke, its heating efficiency, duration of fire etc. compare fabourably with other fuels. It is now found possible to use small coals upto a low limit of 3 mm.

It is now well-known that the liquid and gaseous fuel resources of the country are limited. In the case of liquid fuels, due to inadequate reserves and negligible rate of growth of production, the gap between demand and availability will become increasingly more and, as a result, the imbalance may be as high as 40-45 million tons by 1980. Till now, no effort and very little thinking has been done to bridge this gap or to minimize it except by import. This would obviously impose severe strain on the country's economy and the expenditure involved in the import of oils alone may increase to even Rs. 3000-5000 million per year in terms of foreign exchange within a decade. Apart from liquid fuels, the demand of gaseous fuels, for which the reserves are also meagre, is expected to rise with the growth of industrialization and standard of living. As a solution to these future energy problems, A. Lahiri[10] and D. K. Mukherjee (CFRI) have given an outline of a few concepts based on processing of indigenously available coal reserves. From an examination of the growth of demand and availability of liquid fuels, it is felt that a beginning may be made with the production of 5-10 million tons of synthetic oils by 1980.

The schemes are broadly based on conversion of two distinctly different categories of coal not only to oils but also to power, gas, fertilizers and other chemicals. These are: (i) tertiary coals of north Assam and (ii) Permocarboniferous coals of peninsular India. The processing schemes have been worked out taking into consideration the differences in the characteristics of these coals and the experimental results so far obtained from bench-scale and pilot trials at the CFRI. The overall conversion programme particularly with respect to the integration of several utilization techniques is conceptual in some respects but complete information for designing of process schemes may be available from the pilot plant trials already projected by the Institute. The basic economic features and the possible ways to make the conversion schemes economically viable have also been discussed.

Session II: At the second session presided over by Dr. K. R. Chakravorty, General Manager Planning and Development Division, FCI Ltd., the following papers were presented: (i) 'Gas for Gas Turbines by Lurgi Pressure Gasification of Coal' by P. Rudolph (Lurgi, Frankfurt), (ii) Synthesis Gas Production by Lurgi Pressure Gasification of Coal' by P. Rudolph, (iii) 'Process Technology of Coal-Based Ammonia Plants by A. K. De and B. Chatterjee (P & D Division, FCI Ltd.), (iv) Coal as a Primary Feedstock for Fertilizer Industry by M. K. Pradhan and G. S. Mathur (P & D Division, FCI Ltd.), (v) Planning of Coal Based Fertilizer by M. V. Krishnaiah and L. M. Joshi (P & D Division, FCI Ltd.), (vi) Problem of Supply of Coke Oven Gas as Raw Material Feedstock to the Fertilizer Plant in Rourkela, by A. N. Bose (Calcutta), (vii) Possibilities of Coke Oven Gas as a Feedstock for Fertilizer and Chemicals, by S. K. Ghosh (H. S. Ltd., Durgapur) and (viii) A Comparative Study of Coal & Naphtha for Production of Nitrogenous Fertilizers, M. Ramacharyulu (R. R. L., Hyderabad).

P. Rudolph claimed that the pressure gasification of coal, which has so far been used in the manufacture of town gas and synthesis gas, is also suitable for use in gas

[9] A Non-Conventional Process for Coke.

[10] Convert Coals for Fulure Energy Needs.

turbine powder plants, where it offers the following technological advantages: high gasification efficiency less water consumption, no by-products disposal, etc. The fuel gas, which is free of dust and alkali, is produced with 90 per cent efficiency and is supplied to the combustor of the turbine. It is possible to desulphurize the gas before combustion. Compressed air is used for coal gasification and gas combustion, thus resulting in a high overall efficiency and low investment costs. The investment costs are low compared to coal-fired thermal power stations although the efficiency of the gas turbine process is less favourable.

In his second paper, P. Rudolph first discussed in details the production of synthesis gas from coal by pressure gasification adopting counter-current operation and fixed bed gasification (750-800°C) from revolving grate gas producers operating under atmospheric pressure. The synthesis gas must have an exactly defined composition and be of optimum purity. A comparison was made between several process schemes for gas conditioning and purification of the synthesis gas with regard to investment costs and overall efficiency.

There is a feeling that the coal-based fertilizer process is outdated and can not compete with the naphtha-based process but now with large capacity single-stream units and steam-driven centrifugal compressors it is possible that the former process can stand—and may some times be even cheaper—against the latter, particularly in inland locations. A large number of gasification processes from coal are in existence but the selection of the right process still depends on the type of coal available, economy of the gasification system and waste-heat recovery and its utilization. A. K. De and B. Chatterjee have chosen two process schemes, viz. one using powdered coal gasification process and the other fixed bed pressure gasification for discussion. With adoption of large size equipment, steam intensive and integrated energy system they point out that the manufacturing cost of ammonia can be brought down considerably.

N. K. Pradhan and G. S. Mathur have assessed the relative position of coal against naphtha, at present the most favoured feedstock, for fertilizer industry in spite of its rising price due to world shortage. The reserves of crude oil are scanty (200 m. tonnes) compared to those of coal (1, 31,000 m. tonnes); moreover, naphtha is in deficit—which will go beyond 2 million tons from 1972 onwards. The increase in refining capacity for improving the supply of naphtha will increase the avoidable import or crude and the alternative, viz. import of naphtha is also not desirable as naphtha can no longer claim as the prime feedstock. The authors have shown that considering naphtha and other feedstocks, like refinery gas coke oven gas, etc. non-coking coal is the most important feedstock. The low price per unit energy in coal, its flexible processing techniques utilizing more indigenous equipments and contribution to the national economy by saving scarce foreign exchange along with other intangible benefits and social overheads make coal an ideal feedstock for fertilizer industry in India.

Installation of more refineries essentially to meet the shortage of naphtha would be lop-sided unless the demand in the country for the other refinery products justify. Even assuming that such a demand exists the refinery location will be on the coast and therefore fertilizer units based on naphtha would then to be located near the coast. The fertilizer movement from these units will be inland with the result that the supplies would be irregular and cost more due to freight charges. While ruling out such a possibility the alternative would be coal which is abundant and available at many places in the interior. M. V. Krishnaiah and L. M. Joshi have highlighted the major considerations which enter into the planning of coal-based fertilizer units and their special features. The success of such a unit will depend upon the following factors: location, capacity, process routes, transportation of equipment, manpower and product distribution.

The low ash, high hydrogen content and high tar yielding Assam coals, having reserves of the order of 3,000 m. tons, deserves consideration for use as an ideal raw material for fertilizers in view of the limited indigenous resources of naphtha and natural gas. As an alternative proposal to the coal-power complex suggested earlier, M. S. Iyengar (R. R. L. Assam) proposed a fertilizer project comprising the following two distinct processes (i) devolatilization of 2000 tons/day of coal in a fluidized bed followed by processing of the by-products, (ii) gasification of the fluidized char for the production of fertilizers. The complex is envisaged to produce varying quantities of ammonia, phenol, diesel oil, petrol, pitch, ammonium sulphate and urea. The scheme would involve a total capital investment of about Rs. 67 crores to produce 400,000 tons of fertilizer per year, but the capital expenditure could be reduced to only about Rs. 13 crores if the production is restricted to 22,000 tons/yr to meet the requirement of the State alone.

The fertilizer plant at Rourkela, which is based on purified coke oven gas from the steelworks as the raw material, is faced with inadequate and irregular supply of gas, which is proposed to be made up with synthesis gas to be obtained from cracking petroleum naphtha. But the question of maintaining a steady supply of the available purified coke oven gas continues to pose a serious problem. In the opinion of Dr. A. N. Bose, the design of the process of gas purification from deleterious ingredients like nitric oxide gums, benzol, hydrocarbons, H_2S and HCN after compression to 13-14 kg./cm² in 3 stages, which results in deposition of massive amounts of sludge containing corrosive ingredients inside the compressors, in the gas pipes and the purification units thereby hampering smooth running of the plant and culminating in interruption of the process itself, is seriously at fault and requires radical modification.

The processes available for using coke oven gas for fertilizer manufacture are (i) separation of hydrogen by fractionation, (ii) partial oxidation of hydrocarbons before and after separation of hydrogen and (iii) steam reforming of the hydrocarbons after separation of hydrogen. The first process requires no additional air separation plant (like the partial oxidation one) while the second and third require the substitution of the fuel gas for use in mills and steel melting shops. The first process is the simplest and best in a steel plant as it enriches the fuel value of the coke oven gas and produces low cost ammonia considering utilization of by-products hydrogen; its ammonia capacity is in the range of 400-450 t/day of a gas flow 66000 M³/hr of coke oven gas and economic size is about 100,000 te/yr of nitrogen. The surplus by-product nitrogen from the steel plant's air liquefaction plant will be utilized in each of the three processes. In the opinion of S. K. Ghosh, a fertilizer plant attached to the Durgapur steelworks is quite feasible. This air liquefaction plant could be expanded to 250 t/d of oxygen, which will make 850 t/d of nitrogen available. The latter can be used to make 100 t/d ammonia.

M. Ramacharyulu has compared coal and naphtha as raw materials for the production of ammonia synthesis gas by pressure gasification and steam reforming

methods respectively and has shown that coal can become competitive with naphtha when the ratio of their price per unit heat is about 0.5.

Conclusions: The following are the noteworthy conclusions arrived at the end of the second session: (i) In India at suitable locations, coal-based fertilizer factories can be as competitive as those using other feedstocks; (ii) there should not be any preference to one raw material only; the selection of raw material should depend on availability, economics, location, etc. and should be indigenous; (iii) considering our dwindling foreign exchange, capital formation for this vital industry should be on a self-reliant basis; it should be so planned that no recurring foreign exchange for imports of basic raw material or intermediates is involved; (iv) the case for a coastal plant can be justified only on the basis of export of finished products if it is essential to import raw materials. In the present context of shortage of fertilizer in the country the former does not arise, and in the national interest the latter is unjustified. Again on grounds of strategy on distribution logistics also coastal plants have a restricted area of distribution as compared to interior locations, where distribution can take place in all directions; (v) while working out economics of plants on different feedstocks, the costs of different feedstocks should be evaluated on real costs to nation without taking into account subsidies, duties and taxes. If real national cost is worked out, the preference for indigenous raw materials will be self-evident.

Session III: At the third session, which was presided over by Dr. Tuhin K. Roy, the following papers were read: (i) 'Developments of By-products of Coke Ovens as Raw Material for Organic Chemicals Industry' by A. N. Bose (Calcutta); (ii) By-products of Coal Carbonization in Relation to Development of Chemical Industry' by A. N. Basu & N. G. Basak (CFRI); (iii) 'Naphthalene—a New Field for its Use in the Preparation of 1—Naphthyl—Acetic Acid' J. N. Kapoor & J. M. Sarkar (P & D Divn., FCI Ltd.); (iv) Some Aspects of Coal-based Chemical Industry by D. P. Agarwal & R. Vaidyeswaran (R.R.L. Hyderabad); (v) Coal Chemicals in Eastern Region by S. Banerjee (Durgapur Chemicals Ltd.); (vi) Planning Carbo-- and Petro-Chemicals Projects in India by A. Lahiri (CFRI).

Coal tar and coke oven gas constitute the principal source of the five primary hydrocarbons, viz. benzene, toluene, xylenes, naphthalene and anthracene, and therefore, in turn, of the organic chemicals, dyestuffs, pharmaceuticals, plastics, synthetic fibres, etc. till recently. The rise of the petrochemicals industry after the second World War resulting in economic production in bulk of benzene, toluene, xylenes, etc. from it has led to the decline in importance of the by-products coke ovens as the primary source of the above raw materials. According to Dr. A. N. Bose, it has become imperative to review the prospects of coal chemicals and lay guidelines for their further development keeping in view of the progressive expansion of the iron and steel industry with corresponding increase in coal carbonization capacity and enhanced production of by-products.

Among the primary products from tar, the demand for road tar and pitch is likely to increase. There is already a steady demand of road tar as such or in combination with bitumen. Research and development of new outlets for pitch should lead to considerable expansion of their demand. As regards pure products, production of naphthalene requires to be maximized for important classes of dyestuffs and that of pyridine bases be taken up immediately to provide the essential raw materials for the dyestuffs and pharmaceutical industries. For augmenting the yield of naphthalene, hydrocracking of tar oils at high temperatures and high pressures can be considered subsequently. Further, manufacture of other sophisticated materials, like beta-methyl naphthalene and acenaphthene, can also be taken up. Regarding benzene, toluene and xylenes, the over-increasing demand for benzene would render their recovery essential. The coal chemicals industry should face the challenge of producing BTX in a better quality and lesser cost with diversification of the range of production of benzol products.

The organic chemical industry is very much dependent on steel plants where large quantities of coal are carbonized. Among the four by-products viz. ammonia liquor, tar, gas and benzole, the last three form the basic for the chemical industry. The demand for benzene and naphthalene is increasing rapidly and with correct wash oil and proper scrubbing temperature, benzole recovery can be almost doubled. Similarly, by catalytic hydrocracking crude benzole can be directly converted to pure benzene thus dealkylating the toluene which is surplus. Among xylenes, para and ortho are in demand while meta has little use. According to A.N. Basu and N. G. Basak, the present recovery of many of the hydrocarbons is inefficient. They indicated some of the research work carried out at CFRI on development of improved processes for recovery, purification and synthesis of valuable chemicals, such as benzaldehyde and benzoic acid from toluene, conversion of m- and p-xylenes into ortho- form, refining naphthalene by organic solvents, conversion of alkyl naphthalenes into pure naphthalene by catalytic hydrodealkylation, recovery of over 95 per cent anthracene from anthracene oil, catalytic oxidtion of anthracene into authraquinone, recovery of tar acids from coal tar oils, coversion of higher tar acids to more useful lower ones, conversion of gamma picoline into isonicotinic acid hydrazide, nicotinic acid from quinoline, synthesis of cynopyridine, etc. In the end, A. N. Basu suggested the formation of a separate agency to collect primary crudes from the steel plants and pooled in a centrally located unit where their secondary processing could be undertaken.

With the discovery of plant growth regulating characteristics of some naphthalene derivatives, naphthalene has acquired a new importance as or source of agricultural chemicals and studies have been made elsewhere in India on the growth regulant action of 1-naphthyl acetic acid, which is a costly, imported chemical. J. N. Kapoor & J. M. Sarkar have studied the preparation of this chemical via acylation of naphthalene to 1-naphthyl-methyl-ketone and conversion of the same to corresponding aimed followed by hydrolysis of the latter, which is highly promising.

D. P. Agarwal & R. Vaidyeswaran, after discussing the present position of the coal chemicals industry, indicated the work carried out in their laboratory on the processing of some by-products of carbonization for the production of agricultural chemicals, antiseptics, antioxidants, liquid fuels, etc., such as chlorination of xylenols to get a mixture of chloroxylenols of the individual 3, 5 xylenol, production of antioxidants like alkylated phenol, cresol, xylenols and the separation of phenols, recovery of dihydric phenols from the effluents of low temperature carbonization, dealkylation by thermal or hydro-cracking using suitable catalysts of high boiling phenols to get simpler phenols, catalytic hydrogenation of benzene to cyclohexane for which catalyst has been developed, preparation of suitable binders for bri-

quetting of coal, char and fines from tar and pitch, hydrogenation of low temperature tar fractions to liquid fuels, etc.

The requirement of the principal raw materials used in organic chemical industry and their production (given in brackets) from coal carbonization by 1971 are estimated as follows: benzene 133,000 tons (50,000), toluene 6000 (16000), xylene 37,000 (5000) and naphthalene 20,000 (15,000). The balance may be met from petrochemical industry. Other valuable by-products of coal carbonization are pyridine, ammonium thiocyanate, styrene, indene, anthracene, phenol, cresol, picoline, etc. Statistics indicate that some of the basic coal chemicals, like phenol, pyridine, xylene, cresol, toluene etc., are imported in large amounts while others like aniline, anthraquiuone, b-naphthol phthalic anhydride, maleic anhydride nitrobenzene, amino-phenol etc. which can be easily synthesized here, are also imported. If from the present coal carbonization plants, the by-products are fully recovered there will be no need to import the above chemicals except perhaps phenol, which is now also manufactured via chlorination of benzene followed by hydrolysis in Durgapur Chemicals Ltd. S. Banerjee has also shown that there are possibilities of further development by recovering some of the important by-products of coal carbonization-cum-tar distillation industries which are at present lost.

The urge for setting up of chemical industries based on petroleum resources in the country gained impetus on the presumption that production of naphtha will continue to be far in excess of demand and coke oven products will be unable to meet the market requirement in quality and quantity. In terms of real estimates, considering the actual requirements of nitrogenous fertilizers when at a sub-normal dose as practised now, the country possesses enough capacity to consume the quantity of naphtha feared to be surplus or indisposable. It is, therefore, not surprising that instead of being surplus as predicted only a few years ago, the availability of naphtha is now felt to be insufficient even to meet the requirements of the fertilizer projects already licensed in the Fourth Five Year Plan. To overcome the crisis, the Government is now thinking of producing at least about 25 per cent of the future requirements of nitrogenous fertilizers from coal, a proposal which should have been realised long ago. Thus, the experience gained in case of fertilizer industry may be taken as an example calling for caution in planning of the entire organic chemical industry and especially the aromatic chemical industry based on petroleum refinery products.

While a beginning has been made for establishing a sizeable petro-chemical industry in this country which will no doubt lead to a spurt of further demands of raw materials and intermediates, Dr. A Lahiri in presenting his paper made a plea for taking a balanced view for developing petro and carbo chemical industries, based on indigenous resources especially utilising by-products of pyrolysis of coal. As a corollary to this approach, carbo-chemical industries should be actively sponsored especially in the eastern region of India where oil and coal refineries can be planned with advantage to both, the latter being especially suitable for development to aromatic based chemicals as well as hetero chemicals containing nitrogen. Among the products to be developed highest priorities should be given to agro-chemicals and industrial intermediates which can support small/medium scale chemical industries throughout the country. The need for research and development both for adaptation of imported know-how and for offensive research development was stressed.

Fertilizer Industry Round Table* 1967

The 17th Annual Meeting held in five sessions discussed many points touching the fertilizer industry. Some speakers talked about the plant operations while some referred to air pollution problem. An account was given of high analysis fertilizers. Much discussed problem whether sulphuric or nitric phosphate also found place in debate and its agronomic and economic values were discussed at length.

The first session started under the moderatorship of Dr. Vincent Sauchelli. Mr. Charles, T. Harding surveyed the past of the fertilizer plant operations and gave the glimpses of the future of the fertilizer industry. He predicted that the demand for higher analysis will certainly continue. Larger percentages of the tonnage will be moved in bulk or liquid forms. Even though the bagged fertilizers will decrease in percentage of total shipments, all existing conventional plants will have to be used for mixing, storage and shipping of bulk and bagged goods. The blend and liquids will take care of the increased consumption. Larger producing units for the basic materials will be built for more economical production. The avenues of distribution will be the blend plants with liquid facilities, farm service centers as well as warehouses. If the sulphur shortage results in increased use of nitric acid process or other forms of APS production, some rather large mother plants built in high consuming areas will come up. The more and more fallow land will be tilled on a profitable basis and will consume considerable plant materials.

One delegate pointed out the effect of pill on the population with which the demand of fertilizers is keyed. As it is lately found that during the last decade there is a downward trend in population growth which has forced the demographers to revise their estimates. This will necessiate the revision of fertilizer demand also and to this Mr. Harding agreed.

Air Pollution: The next two papers dealt with a very lively subject i.e. air pollution by effluents. Besides health hazards these effluents cost much in terms of product loss also. Mr. J. A. Hammett gave an account of the tests carried on particulate matter, free ammonia, ammonium chloride and fluoride in granular fertilizer. According to him the largest material loss from a dryer is usually free ammonia or dust, the average free ammonia loss being about 53 lbs./hr. and the average dust loss about 38 lbs./hr. Although the concentration of ammonium chloride discharged from the ammoniator is not very high in lbs/hr. it appears as a very heavy, white fume. This fume or mist, is approximately 1 micron in diameter and is very difficult to remove by scrubbing. It was determined by pilot plant test that a concentration of .001 grains of Ammonium Chloride/ft^3 is invisible to the eyes in most atmospheric conditions. This concentration was obtained by the Venturi type-long throat-high differential pressure equipment. A high differential pressure of 54 inches of water was used in this system. The gas volume through the scrubber was 4600 C.F.M. Although the efficiency of the ammonium chloride removal was only 91.0%, the scrubber removed ammonium chloride down to .003 grain/ft^3. The removal of free ammonia is not efficient, but this can be corrected, said speaker, if necessary by maintaining the pH of the scrubber water at less than 7.0.

Then Mr. John S. Lagarias gave an insight into the complexities of sampling

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stack emmissions and discussed the influent and emmission problems, sources of measurements of gases and aerosols, effect of polluants particularly fluoride, ambient air measurements, material balance for fluorides etc.

Mr. J. M. McManus gave an account of the performance of the air classifier manufactured by the Buell Engineering Company. He narrated the operating principles and details of the Buell gravitational classifier.

Solution Mining: Mr. G. J. Lambillotte of Kalium Potash Plant told how geography and geology of Saskatchewan forced his company to go for solution mining. According to him the availability of the vast volumes of dependable and relatively thick deposits of potash was the foremost advantage for solution mining. Higher K_2O percentage, dependable quality, and solubility of product was an added advantage. Competetive economics, experience and free choice for an industrial location forced them to go for solution mining. Then he compared the costs of shaft mining and solution mining. He pointed out that shaft mining is favoured because of lower fuel costs, less investment above ground, more readily available cost data, low water consumption. But he stressed that factors like lower manpower requirements, less investment underground, faster implementation of capital (a solution plant can be built in about 18 months), low chemical consumption, wider market participation involved in solution mining has an edge over shaft mining. With this paper the first session ended.

Second session touched the subjects like citrate insoluble phosphate in ammonium phosphate production, high analysis fertilizer and ended with a discussion on a burning topic, sulphur—*Quo Vadis?*

C.I. in Ammonium Phosphate Production: The presence of citrate insoluble phosphate (C.I.) material in ammonium phosphate production results in an economic loss to the manufacturer, since his product analysis is based on the per cent P_2O_5 available and not on the total P_2O_5 present in the final product. Mr. C. M. Davis of the J. R. Simplot Company evaluated the citrate insoluble content in the various samples and presented his findings. Unavailable P_2O_5 values in the citrate insoluble fraction actually has nutrient value to the growing plant. Greenhouse experiments indicated that the C.I. material actually is a valuable fertilizer material. It was found that extended contact with the citrate extraction solution significantly reduces the reportable C.I. fraction in a given sample. It was also found that the material which shows up C.I. in ammonium phosphates is not tricalcium phosphate, the material for which the citrate solubility criterion was developed. As regards the cost author made the following calculation for a plant producing 500 tpd 16-48-0 for a 330 day per year operation. Assuming phosphoric acid production 160,000 tons per year P_2O_5 with a cost of $ 65.00 per ton based on a rock cost of $ 5.00 per short ton and sulfur at $ 39.00 per long ton, the cost of C.I. is $ 72,280 excluding the value of the nitrogen which is lost in the citrate insoluble fraction.

Manufacture of 17-17-17 Fertilizer: Triple 17 whose P_2O_5 content is over 90% soluble in water is applied to fields of beet roots and is used as top fertilizer for wheat. The raw materials required for the manufacture of per metric ton of 17-17-17 fertilizer by the Pechiney-Saint-Gobain Compound-fertilizer Process is as follows:

HNO_3 (100%)	..	315 kg.
Anhydr. NH_3 (gas or liquid)	..	130 kg.
P_2O_5	..	173 kg.
KCl (as 60%K_2O)	..	288 kg.
Enrobant-Coating agent	..	15 kg.
Electricity	..	30 kWh.
Fuel Oil	..	14 kg.
Ammoniation Molecular ratio	$\frac{NH_3}{H_3PO_4}$	= 1.05

Ammonium nitrate liquor is prepared by feeding ammonia and nitric acid (previously heated by reaction fumes) in a thermosiphon neutralizer where the reaction takes place under atmospheric pressure. At this stage the concentration of the solution is 90-92% ammonium nitrate. This solution is next concentrated to 97% in a falling film evaporator under atmospheric pressure. Heating is by steam on the outside of the pipes, and by hot air current inside. The temperature never exceeds 150°C and consequently does not give any operating hazards.

Ammonium phosphate is prepared continuously in an agitated stainless-steel saturator equipped with four ammonia nozzles. Though ammonia can be used as a gas or as a liquid generally it is used as a gas in order to evaporate as much water as possible in the tank especially since the evaporation of ammonia contributes to the conditioning of air in the fertilizer cooler. The molecular ratio NH_3/H_3PO_4 is kept at 0.6 during the ammoniation and never exceeds 0.7 to maintain a high fluidity of the slurries; the make up of ammonia to the ratio 1.05 is made in the granulator.

The granulation is carried out in a rotary drum which receives—the ammonium phosphate slurry fed through an open chennel; the ammonium nitrate liquid delivered by a perforated pipe. The liquor could be introduced if desired into the ammonium phosphate reactor the solid products: KCl and the recycled product through a feed pipe at the inlet of the granulator; the liquid anhydrous ammonia through a row of nozzles immersed in the bed of the material during the granulation. Then it is followed by the operations like drying, screening, grinding, cooling, coating, storage and bagging. Systematic control over moisture content, sphericity, crushing strength, hygroscopicity, coating etc. is necessary.

7-28-28 Granular Fertilizer: Mr. John Surber of International Minerals and Chemical Corporation gave an account of the series of pilot plant tests carried out to study the 7-28-28 granular fertilizer. Based upon the data that were gathered at the pilot plant, it was concluded that both chemically and physically satisfactory product can be made from coarsest potash with over 70%, plus 35 mesh material. There is very little advantage gained by using a finer form of potash or by introducing the slurry to a pugmill prior to the drum granulator. Phosphoric acid with 64.9 per cent P_2O_5, on a bone-dry basis, is required to make a 7.3-28.2-28.2 fertilizer with 60.5 per cent (K_2O) potash. This is equivalent to 54 per cent P_2O_5 phosphoric acid, with 17 per cent water. The quality of wet process phosphoric acid is not critical regarding granulation efficiency.

Ammoniation and Granulation in the Blunger: Mr. D. W. Leyshon and Q. D. Bowers made an up-to-date review of the concepts of ammoniation and granulation in the blunger. They narrated some of the characteristics of the blunger and discussed the particular field of application and presented some performance data.

The blunger may be described as a reactor for producing a fluidized bed, wherein recycled fines, solid raw materials, wet slurry, and ammonia are thoroughly mixed and reacted. Blungers have been demons-

trated to be very effective for the granulation of grades which are sticky and tend to produce excessive quantities of oversize. Slurry process triple superphosphate and high nitrogen grades using urea or ammonium nitrate are particularly suited to blunger granulation. In addition, it has been demonstrated in several recent installations that high degrees of ammonium can be very effectively carried out in the blunger because of the deep, violently agitated bed which makes it possible to use the heat of reaction to evaporate large quantities of water. It is, therefore, possible to produce DAP and DAP based NPK grades at high rates using the blunger. Preparing hard granule containing low moisture, author believed, is also possible with the help of blunger.

He further informed the gathering that over 50 blungers are used in over 30 plants throughout the world to manufacture 5 million tons of fertilizer each year. At present there are under construction 9 fertilizer plants in countries like England, India, Japan, and Louisiana employing 21 Dorr-Oliver blungers, with a total capacity in excess of 2.5 million tons per year of fertilizers.

Sulphur, Quo Vadis?: Sulphur is a vital mineral used in the production or processing of very nearly every product of our daily life and the per capita use of sulphur is a good indicator of the living standards of the population of a given country. Half of all sulphur is consumed in the production of fertilizers which are so essential in modern man's quest for more food in view of the anticipated ever increasing growth in the world population. A severe or prolonged shortage of sulphur, such as we are experiencing today, may endanger corporate investments of the sulphur using industries, affect the economic growth of a country, imperial defence requirements, and jeopardize the entire world food production programme. It was but natural for the meeting to take the congnigance of this vital problem. The sulphur shortage problem was analysed in its proper perspective by Dr. Serge L. Levitsky, Manager of Market Research, Texas Gulf Sulphur Company. The amount of sulphur required to produce 14.7 million tons of P_2O_5 would be in the heighbourhood of 10 million ton. The Tennessee Valley Authority which in 1965 conducted a survey estimated that existing capacity would increase by more than 60%, between 1965 and 1970, from 12.2 million tons of P_2O_5 to at least 19.4 million t ons of P_2O_5. Currently, the anticipated capacity for 1970 is even higher over 23 million metric tons of P_2O_5. If we add to this figure the sulphur required for the manufacture of ammonium sulphates and of other fertilizer materials, and assume that non-fertilizer uses of sulphur will continue to grow at the current modest annual rates, total demand for sulphur in the Free World in 1970 would reach almost 32 million tons. This is corroborated by computing the per capita consumption of the sulphur which works out to be over 31 million tons by 1970.

Then author quoted the production and consumption figures of the free world (U.S.A. and Mexico) to show the continuous deficiency. This continuous deficiency in author's opinion can be met only if (1) new reserves are discovered; (2) presently known but still undeveloped reserves are brought into production; and (3) other, highcost sources and forms of sulphur are tapped and developed. About discovering new reserves the author was pessimistic and pointed out that inspite of sizable amount of money spent no commercial feasible deposit could be discovered. About the second proposal he said that there are no longer any known large undeveloped reserves of low-cost sulphur left. Attempts are being made to produce sulphur from known, but hitherto uneconomical deposits like Frash sulphur, sour natural gas and petroleum refinery gas.

There are, however, vast known reserves of higher cost sulphur available in many parts of the world such as pyrites and other forms of non-elemental sulphur, as well as certain types of elemental sulphur. The costs of extracting and transporting sulphur from these sources are very high, requiring heavy investment on the part of producer and consumer alike. In contrast, the size of the reserves makes these forms of sulphur eminently suited to become a permanent source of supply for decades to come. Then author concluded his speech by saying that the effect of sulphur shortage is still uncertain. But a significant portion of the demand may still remain unsatisfied and the products of which sulphur is a major raw material will affect. The allocation program has and will have some desirable effect on consumption of sulphur. And side by side as has shown an increase in the price stimulates new production e.g., even gypsum is being investigated as a possible source of economical sulphur today. With this new hope of meeting the sulphur shortage gathering adjourned till third session.

Sulphuric or Nitric-Based Phosphates? An Economic Evaluation: The fertilizer phosphate industry, based on sulphur as a raw material in the acidulation of phosphate rock, is feeling the effects of rising prices of sulphur and short supply. It is therefore, natural for the phosphate industry to explore the claims of alternate methods of preparing available P_2O_5 from phosphate rock. One of the more popular successful alternates is to acidulate the rock by nitric acid. The method has been successfully employed in many European countries. But the economic and agronomic aspects of the nitrophosphates which is the prime concern of industrialists and farmers alike are still much debated.

A wide-spectrum direct economic comparison of fertilizers made by both process poses a main difficulty as the end products are not the same e.g. Odda type nitric acid plant aims at producing much more nitrogen than phosphate, where as for straight DAP the opposite is true. An attempt to compare the costs of various plant nutrients was made by Mr. Bixby of the Sulphur Institute. These costs are based on the assumption of equal outputs of N and P_2O_5 though this tends to give an economic advantage to the Odda process by using it as a standard and adapting the conventional processes to the relatively inflexible N/P_2O_5 ratio inherent in the overall Odda process.

A product with a high content of P_2O_5 (DAP, triple phosphoric acid) can be made on a site where low cost phosphate rock is available. This product can then be shipped economically to wherever it is to be used. At the point of use, nitrogen and potash containing products made at, or convenient to, that site may be added to it or added to the soil independently of it, as is the case with anhydrous ammonia. The location of an Odda type nitric phosphate plant, on the other hand, is limited to the most economical site of nitrogen production. This is because it produces substantially more nitrogen than P_2O_5, and nitrogen is therefore the dominent economic consideration. Nitrogen is everywhere, but the cost of the necessary hydrogen will vary with location. As the product and co-product, taken together, are not of sufficiently high analysis to justify shipping great distances, the plant must be near the site of product use and the phosphate rock must be shipped to that point. The P.E.C. process is less dependent on the site of nitrogen production than is the Odda process. Nevertheless,

nitrogen cost of P_2O_5 in the product, whereas for the conventional sulphuric acid-based processes, P_2O_5 is independent of nitrogen cost.

Six conventional processes were selected for comparison and their data presented is as follows:

INDEX OF PLANT NUTRIENT COSTS OF VARIOUS PROCESSES (ODDA = 100)

(Plant Capacity = 250 tons)

Sulphur cost/ton	PEC-2 (14-14-0 grade with 30 WSP)	PEC-3 (20-20-0 grade with 30 WSP)	DAP-1 (28.5-28.5-0 grade with 100 WSP)	Triple-1 (23-23-0 grade with 87 WSP)	Normal-1 (13.9-13.9—0 grade with 98.5 WSP)
$ 35	106	115	106	99	90
$ 42.50	107	117	108	101	92
$ 50	108	119	111	104	94

WSP—Water Soluble Phosphate

An Agronomic Evaluation

Dr. G. R. Burns presented the agronomic value of the nitrophosphates, a controversial subject. In using any fertilizer its properties like water solubility, particle size, N: P_2O_5 —ratio, form of contained nitrogen and placement of fertilizer in the soil are most important. Before plant can use the fertilizer it must be water soluble when applied it with the soil. Sulphuric acid/phosphoric acid based phosphate fertilizers are 95-100% water soluble while nitric acid based fertilizers are generally 50% or less water soluble though water solubility can be increased at the greater manufacturing cost. There is a strong interaction between particle size and water solubility in terms of plant response; 12 to 50 mesh particle size is optimum and particles coarser than 12 mesh size are less effective.

The ratio of N: P_2O_5 and the form of nitrogen in the phosphate fertilizer are very important. High nitrogen content in nitrophosphates makes them unsuitable for some legumes and plants like soybeans, alfalfa. Because of the nitric-nitrogen content in nitrophosphates they are not best suited for paddy rice. Under waterlogged conditions, much of the nitrate nitrogen may be reduced and lost as a nitrogen gas. The author drew the conclusion that if nitric phosphate is granular say 6-14 mesh, and contains less than 50% of its phosphorus in a water soluble form, then a few farmers can adopt nitrophosphates without losing their profits.

Variation in Composition of Phosphate Ores and Related Reactivity

It is a common experience of operators of superphosphate production that the reactivity of rock differs sample to sample. Apatite varies widely in chemical reactivity and thermal stability. James R. Lehr of TVA gave an account of the results of 145 phosphate rocks of high grade apatite concentrates. They studied the chemical characteristics and crystallographic studies like X-ray, infrared, petrographic etc. Based on these studies, thermal stability study revealed that one third to one-half of the total weight loss, representing organic matter and adsorbed water, occurs below 500°C, without change in properties of the apatite. Above 500°C., however, the additional weight loss corresponds closely to the combined amounts of CO_2 and F expelled from the carbonate apatite. The total weight loss for each phosphate rock thus is directly propertional to the amount of (CO_2+F) initially substituted for PO_4. There is decrease in thermal stability of the apatite with increasing degree of substitution. Highly substituted apatites begin to alter between 500°C and 600°C., whereas those with the least substitution are stable to temperatures between 700° and 800°C. Results indicated that homogenity of the apatite mineral is not a contributing factor to difficulties in its dissolution. Chemical and crystallographic studies of phosphate rock residus after successive stages of dissolution in dilute (2%) nitric acid showed no changes that would indicate a selective dissolution process. Similarly, phosphate rock residues recovered from gypsum filter cakes had the same chemical and crystallographic properties as the initial rock, but the particle surfaces had become sealed off by calcium sulfate coatings.

Bulk Blend Economics

"If blend plants are properly operated, well planned, located in right position, and backed very adequately by a sales force they can return a good net profit to the organisation" observed Mr. Henry Plate, former manager of "Bulk Blend Plants" for Agway, Inc., Syracuse N. Y. The prerequisite for blend plants are as follows: The blend plant must have a potential of 3,500 tons (50 unit tons), this would be the equivalent of 7,000 tons of 5-10-10. Blend plants must have a rail siding to handle incoming materials, although outgoing materials go by truck. A 600 to 800 ton storage capacity is reasonable and necessary for this operation. Separate unloading and loadout system is required so supplies can be replenished while shipping. The capacity of these unloading and loadout legs should be 60 tons per hour in order to keep up a 20 ton per hour output of the plant. Man power requirement of a plant operating at 2,000 tons per year and under is about 1.1/4 men per year while for 2,000 to 3,000 tons about 1.1/2 men and for over 3,000 tons two men. (This manpower requirement exclude the need for spreader truck drivers). The last requirement is a uniform mixing of the ingredients without grinding of the particles. Then he gave the plant and operating costs. In future, author con-

BLEND PLANT COSTS

	Horizontal	Vertical
Land & Improvement	$ 6,000	$ 6,000
Building	25,000	63,000
Equipment & Install	19,100	
Electricity	3,400	
Siding	12,500	12,500
Engineering	1,400	1,400
Misc.—Water, Legal	2,600	2,600
Total	$ 70,000	$ 85,500

OPERATING COSTS
(Exclusive of Spreading)

	2,200 T (Vert.)	2,200 T (Horiz.)	4,300 T (Horiz.)
Salaries & Cost-Mgr.	$ 7,800	$ 7,800	$ 9,000
Salaries & Cost-Part Time	800	1,500	5,000
Travel	600	600	1,000
Maintenance	510	950	2,600
Fuel, Light, Power	320	320	740
Demurrage	1,800	90	3,500
Inventory Adjustment	600	600	1,200
Telephone	420	420	860
Rent, Ins.	9,350	7,800	8,300
Payloader	—	850	900
TOTAL	$ 22,200	$ 20,930	$ 33,100

cluded that horizontal plants are preferred to vertical plants.

Recent Applications of Nitric Phosphate Processes

Limited water solubility, grade flexibility, the overall nitrogen to phosphate ratio, storage properties and process complexity are some of the said disadvantages which keep many fertilizer manufacturers away from entering into nitric phosphate field. But none of these objections are sufficiently valid said Mr. Clem B. Giles of C & I. Girdler, Incorporated a company backed with the experience of building 20 nitric phosphate plants around the world. He argued that now it is possible to manufacture a fertilizer with 90% P_2O_5 water solubility. It is sufficiently demonstrated that nitric phosphate process can produce wide varieties of nutrient ratio and grades. Regarding the problem of the overall nitrogen to phosphate ratio, until calcium nitrate is commercially converted back to nitric acid, this point is bound to remain a problem for those companies which are not interested in becoming basic in nitrogen. On the other hand, the trend of nitrogen fertilizer producers to become basic in phosphates is bound to induce the phosphate producers, in turn, to become basic in nitrogen. And the fact that nitric acid is used twice when over-all nitrogen P_2O_5 balance permits it, is one of the major advantages of the nitric phosphate approach.

About the storage problem author said that though the product is more hygroscopic than DAP or triple super, the bulk shipment of product under variety of conditions solves this problem. Moreover, he pointed out that most bulk blends today contain urea or ammonium nitrate and are essentially similar in this respect to nitric phosphate. As regards process complexity, author emphasised that there is no difficulty in switching grades and in many cases grades change can be accomplished as fast or faster than in mixing plants.

Then Mr. J. E. Carr of Denver Equipment Company gave an account of the new developments in automatic sampling. He described in detail the new development viz. bigger sample mechanisms, better chute samplers or stream analysis; experimental design methods and pointed out that these new developments are being applied to projects.

Analytical and Quality Control Programme

There was a panel discussion on this subject headed by J. R. Archer, Quality Control Manager of IMC. The first panel member described how automation has significantly improved the quality control programme of the company and eased the analysts' work in addition to giving accurate results. The second speaker gave an account of an automatic four channel analytical system for the simultaneous determination of P_2O_5, K_2O, ammoniacal nitrogen and nitrate nitrogen in complex fertilizers, the accuracy and the precision of which has been shown to be comparable to standard techniques. Consideration for the use of such systems on a totally automatic basis where sample would be obtained, processed and analysed, totally independent of human intervention has also been discussed. The analytical data it was suggested, then could control the plants to regulate the various nutrients being fed into the process.

Dr. E. D. Schall talked about automation in fertilizer laboratory. He referred to the atomic absorption, a analytical technique and specific ion electrodes as promising tool for the fertilizer laboratory. This was followed by Dr. James F. Marten's review on "Applications of Automatic Analysis in the Fertilizer Industry". This review covered the applications of continuous chemical analysis throughout the fertilizer industry. Review contained applications that have been proven in practice both as technically valid and economically sound.

40% Water-Soluble P_2O_5 in NPK

Dr. J. Jung started the last session saying that 40% water-soluble P_2O_5 in NPK is adequate. "We are thus led to the conclusion" said he, "that under agricultural conditions in Germany only on a small proportion of the soils in use can phosphate fertilization be expected to influence plant yields directly. The same applies to many soils in other parts of the world, whereas in areas with a low level of fertilization one can expect both the soil's phosphate pool to be further built up as the result of continued fertilization and the immediate effect of the phosphate fertilizer to become decreasingly important. Although the value of the acidulated fertilizer phosphate for the plant will not be diminished, the quest on whether a phosphate fertilizer which is completely soluble in alkaline ammonium citrate solution would contain a water-soluble portion of 30 or 50% will have to be regarded as academic and not of any appreciable significance for fertilization in practice. For the time being, however, 30-40% water-soluble phosphate portion in an otherwise completely ammonium citrate-soluble nitrophosphate should not be dispensed with as a safety factory, since experience has shown that with granular NPK fertilizers this guarantees optimum action in a wide range of variations in soil, climate and plant species".

This conclusion was substantiated by the results of 125 field tests carried over ten years in various regions of West Germany soils which were as low in phosphate as possible. In these tests the NPK fertilizer Nitrophoska was compared with that of completely water-soluble straight phosphate fertilizers. No difference between the actions of completely water-soluble phosphate and nitrophosphate with a 35% water-soluble phosphate fraction has been established.

Nitrophoska

Dr. Gero Leuth narrated the story of 40 years of NITROPHOSKA, a BASF

trade-name used since 1927 for compound fertilizers. These fertilizers contain all nutrients in practically the same ratio in each individual granule. The danger of separation and segregation during storage, transport and application is therefore eliminated. The author gave the following brief description of the present NITROPHOSKA production system.

The coarsely ground phosphate rock is dissolved with 55-60% nitric acid. A special method of operating and a special design of the vessel help to control foam formation. Chilling is carried out batchwise by means of brine. The heat of evaporation of the ammonia required for neutralization and conversion of the calcium nitrate in the process provides the necessary refrigeration. When liquid ammonia is used, the process requires no additional cooling. The separation of the calcium nitrate is carried out in multistage pusher-type centrifuges. By using a special procedure the screens of the centrifuges are prevented from being blinded by sand. The separated calcium nitrate is melted, and converted with ammonia and carbon dioxide, cooled ammonium nitrate being recycled during the process. The ammonium nitrate can be concentrated to 99% by treatment in multi-stage evaporators of a special design. There is no trouble with crusting. The mother liquor from the calcium nitrate separation is mixed with the necessary amount of ammonium nitrate and neutralized with ammonia or with offgases from the urea plant in several stages. Magma is a product whose viscosity is so low that it can be evaporated at temperatures below 130°C to a water-content of less than 8%. This magma, whose N: P_2O_5 ratio is adjusted precisely, is granulated without or with varying amounts of potash to fertilizer of the type 20:20:0, or 13:13:21 or 15:15:15.

Nitrophosphates—Comparative Agronomics and Economics

Regarding agronomics of nitrophosphate Mr. Christopher J. Pratt said that the behaviour of phosphate fertilizers in soils is complex and is affected by (1) fertilizer properties, such as phosphate, water and citrate solubilities, chemical composition and attendant ions, physical properties and particle size range. (2) Soil properties, e.g. moisture, chemical characteristics and pH, physical characteristics. (3) Ambient conditions, such as intensity of application (lbs./acre), pattern and method of application, type and nature of group sown, climatic conditions etc.

Then he laid down various water-solubility Criteria for various crops: (1) Low water-solubility (say O to 33%) suffices for pastures, trees and other long-season crops especially when soils are acidic or neutral and high in residual phosphate. The fertlizer should be of small particle size and preferably broadcast. (2) Medium water-solubility (e.g. above 33 to 67%) is suitable for crops having bushy root systems and a phosphorus uptake which corresponds to the rate of P_2O_5 release. The fertilizer should be of small granule size and evenly dispersed in the soil. The use of phosphates in this category can often be extended over a wide range by applying in conjunction with highly water-soluble "starter" fertilizer and/or maintaining high residual soil P_2O_5. (3) High Water solubility (above 67%, and especially over 80%) is satisfactory for all crops and soils, except where "burning" may be a problem. The fertilizer can be of relatively large granule size (especially on acidic or neutral soils), and is preferably applied in banded or localized patterns.

Then he gave the following comparative production data (table below):

He concluded that the modern processes enable grades containing some 50% of plant nutrients to be made in the form of granules or prills having water solubilities tailored to meet agronomic needs ranging from 0 to 95 per cent. Some of these processes entirely avoid the use of sulfuric or phosphoric acid, which results in an increasing cost advantage in times of rising sulfur prices. The newer processes and their wide product ranges offer considerable manufacturing and agronomic flexibility. In view of the availability of such technology, and the need to insure against limitations being imposed on phosphate fertilizer manufacture by a sulfur shortage, the newer nitrophosphate processes and products can be recommended under appropriate conditions as a good way of meeting

COMPARATIVE NITROPHOSPHATE PRODUCTION DATA

(Calculated on Basis of 1,000 Short Tons Solid N-P per-day)

Process, Product, Co-products	1 Phosphonitric (20-20-0[1])	2 (20-20-0[2]) Odda-Type +600 tpd AN[2]		3 (25-16—0[2]) SO_4 Recycle
Raw Materials, T/T Product		N-P	AN	
Phos. Rock 73 BPL	0.27	0.6	—	0.50
Nitric Acid 100%	0.44	0.43	0.47	0.50
Phosphoric Acid P_2O_5	0.11	—	—	—
Ammonia 100%	0.14	0.15	0.14	0.16
CO_2 100%	—	—	0.20	0.14
Gypsum	—	—	—	0.05
Labor				
Operators/shift	5	5	2	7
Utilities				
Power, kWh	80	53	18	45
Water, M gallons	1	3.5	1.5	20
Steam, M lbs.	—	2	—	3
Fuel, MM Btu	3	0.9	—	—
Miscellaneous				
Coating T/Ton	0.02	0.02	0.02	0.02
Ancillary Items $/Ton, say	1.0	1.0	0.5	1.00
Financial				
B/L Cost $ MM	5.5	6.0	2.5	5.50
Royalties	incl.	incl.		incl.
	[1]) Granulated	[2]) Prilled		

NOTES: Process 1 does not include sulfuric and phosphoric acid in manufacture.
Processes 2 and 3 yield by-product calcium carbonate.
Potassium chloride or sulfate can be added as desired.
Data are approximate and based on U.S. installed plants.

expanding fertilizer needs in both the developed and developing countries of the world. With this consensus the meeting ended.

Boosting up Production in Heavy Water Plant

The heavy water plant at Nangal (Punjab) is designed to produce 14.1 tonnes per year heavy water by the fractional distillation of hydrogen obtained from the electrolysis of water. The enriched hydrogen from the third stage is routed through the heavy water plant where fractional distillation, in stages, produces 100% hydrogen deuteride (HD), which is passed through a catalyst bed to bring about isotopic equilibrium. The mixture of hydrogen, deuterium and hydrogen deuteride is finally fractionally distilled to yield 99.98 per cent or more deuterium. It is then oxidised with purified oxygen in the presence of a catalyst to produce heavy water. The designed capacity of this plant is based on 500 Nm^3/hr. of feed hydrogen, containing 880 ppm HD with a stream efficiency of 8000 hours and 90 per cent recovery. As the synchronisation of maintenance in the heavy water and fertilizer plants is not possible, the effective annual capacity got reduced to 13 tonnes from the designed capacity of 14.1 tonnes. And the actual average production per year during last four years was 10.294 tonnes. The decrease in the production was primarily because of leakages in the electrolysis plant, which resulted in a lower HD concentration in the feed hydrogen gas.

By interpretation of the operating data and from the test runs, it was inferred that the ratio of recycle hydrogen to feed hydrogen could be reduced from design value of 1.5 to 0.79, without affecting the recovery efficiency in the plant. Calculations revealed that the plate efficiencies for the three stages of the primary distillation column, when processing 5400 Nm^3/hr. of feed hydrogen, containing 704 ppm HD range between 35 to 44 per cent. When the HD concentration was increased nearly six times i.e. to 4280 ppm, the plate efficiencies range between 46 to 52 per cent for the same flow without affecting the recovery efficiency. The plate efficiencies at a feed concentration of 704 ppm HD were lower due to under-utilization of the primary column.

It was confirmed through a test run that the feed hydrogen processing in the cold-box can definitely be done to the extent of 8000 Nm^3/hr. or more, without affecting recovery efficiency in the plant. Further the two existing feed hydrogen compressors, which are together rated for 5400 Nm^3/hr at a suction pressure of 100 mm. of water, were found as a result of another test run to be capable of handling the increased hydrogen flow, provided the suction pressure is increased to 0.4 kg/cm^2. It was envisaged to do this by means of a cycloidal blower. The blower along with its drive and other auxiliaries, were procured from M/S Linde (West Germany), at a negotiated price of Rs. 2.74 lakhs (FOB). The installed cost has been within the original project estimate of Rs. 4.2 lakhs. The machine was commissioned in April 1968 and after a few modifications it is running satisfactorily with an average feed hydrogen flow of about 8700 Nm^3/hr. The extra feed hydrogen that is being processed, over and above the hydrogen supply from the third stage of Electrolysis Plant, is taken from the second stage, having a concentration of about 140 ppm HD.

As a result of intensive overhauling in the Electrolysis Plant the HD concentration of feed hydrogen has improved to 780 ppm. This concentration, it is reported is still much below the design value of 880 ppm. With the present lower HD concentration and based on original design of processing 5000 Nm^3/hr. feed hydrogen, maximum annual heavy water production possible, as such, assuming no troubles and in the absence of cycloidal blower, would have been 12.536 tonnes.

[*FCI News*, **6** (6) (1968), 5 and *personal communication from Mr. K. S. Bimbhat, Scientific Officer*, (FCI Ltd. Nangal Unit)

News in Brief

Chemical Removal of Phosphorus From Effluent Wastes

Investigations carried out by the Federal Water Pollution Control Administration, U.S.A. indicate that 90 to 95% of phosphorous recovery from municipal waste waters is possible at a cost of 5 cents or less per 1000 gallons for a 10 million gallon p.d. plant. Two types of chemical/biological system are envisaged by FWPCA. A chemical precipitator such as lime may be added to a primary tank to remove most of the phosphate, prior to the biological aeration stage, which removes additional phosphate material. The alternative method is to add the chemicals directly to the aeration tanks. Iron or aluminium salts are suitable for this technique as they do not impede biological action, and the residence lime provided in the aerator is sufficient for a precipitate to form.

In a specific study carried out by FWPCA at a waste water treatment plant an Xenia, Ohio, using sodium aluminate in a aluminium/phosphorous ratio of 1.8: 1, 85% to 92% phosphate removal was achieved. Treatment with lime results in phosphate removal in excess of 90% and in this case the sludge formed can be recalcined to recover some of lime.

(*Phosphorous and Potassium*, No. 35, May/June (1968), 46)

Purification of Wet Phosphoric Acid With Active Carbon

A recent British Patent (No. 1,103224) granted to Marchon Products Ltd. details a method to remove organic impurities in wet process phosphoric acid with an activated form of carbon. It was shown that even relatively large amounts of organic matter could be removed by allowing the phosphoric acid to come into contact with the activated carbon at a relatively high temperature at least 60°C and preferably above 80°C. In practice, the carbon is used in conjunction with a flocculating agent, unsually of the polyacrymide type, to assist the settling of the active carbon, contact with the acid can be obtained by using a two or three stage counter-current process or by using granulated carbon in a bed or lower. The carbon is made by treating either sawdust or cocoanut shell with a mixture of sulphuric and phosphoric acid and can be regenerated with a caustic soda solution. The removal of the organic impurities can be carried out at any stage in the acid manufacture after the gypsum filtration but is best instituted after the defluoration stage.

(Phosphorous and Potassium, No. 35, May/June, (1968), 47)

Desulphurizing Catalysts

A new desulphurizing catalyst has been developed by the North Western Gas Board of U.K. This special catalyst enables organic sulphur compounds to be removed from hydrocarbons by contacting the latter in the vapour phase in the presence of water vapour at between 350°—500°C. The catalyst comprises Uranaso-Uranic Oxide (U_3O_8) and/or uranic trioxide (UO_3) on a carrier such as alumina. Total uranium oxide content of the catalyst varies between 5 and 10%. Other carriers suggested are silica, Kaolin, magnesium silicate or magnesium, calcium, strontium and barium oxides.

(*Sulphur* No. 75, (1968), 42)

Fisons Fertilizers Ltd., Develops Ammonium Phosphate Nitrate Process

Fisons Fertilizers Ltd. has developed a process for the preparation of ammonium phosphate nitrate melts which involves the ammoniation of acidic mixture containing nitrate, phosphate, ammonium and hydrogen ions and preferably 0.1 to 1.2% water at a temperature between 120°C and 200°C. Ideally a 10% by weight solution of the initial acid mixture should have a pH of 2.2 to 2.8 and a similar solution of the ammoniated product should have a pH of 4.0 to 7.0. If the ammonium phosphate is required as diammonium phosphate, ammoniation must be continued to pH 8.0, but the optimum N: P ratio is 1.75:/ which corresponds to pH 7.0.

One advantage of using acidic mixtures at pH 2.0 to 3.0 is that they can be dried more easily to 0 to 2% moisture than acidic mixtures with pH values outside this range; another is that within this pH range, nitrogen losses, as nitrogen oxides, nitric acid and ammonia, are reduced. Initial moisture reduction, down to 3% may be carried out at atmospheric pressure by boiling, but final drying is achieved at reduced pressures (200 to 300 mm Hg) with passage of air. Normally the acidic mixtures contain between 1.3 and 20% water depending upon the feedstocks and method of preparation, and these melts are dried to the appropriate moisture content using hot air to avoid cooling prior to their introduction into the ammoniation section.

The acidic mixture is carried out at as low a temperature as possible to minimize ammonia losses during cooling; the lowest practicable temperatures are between 150 to 185°C. Normally the reaction is carried out at atmospheric pressure, but higher pressures may be used. The heat evolved during the ammoniation may be controlled. After ammoniation, the ammonium phosphate nitrate melt may be granulated, prilled, converted into flakes and mixed with other. Preparation of the acidic mixture may be done preferably from ammonium nitrate and/or nitric acid and phosphoric acid; sulphuric acid or ammonium sulphate may also be included. Other feedstocks which can be used include monoammonium phosphate, diammonium phosphate and recycled ammonium phosphate nitrate product. Two versions of the process have been given. In the first process phosphoric acid, hot nitric acid and ammonia are fed to the mixing tank together with a large amount of the acidic mixture recycled from the drying tower. The heat of reaction raises the temperature of the acid melt to 177°C and this is then dried with a counter current steam of hot air. After drying 97% of the melt with a moisture content of 0.2% is recycled to the mixing tank, the remainder being fed to the ammoniation tank. Here gaseous ammonia is introduced until the mixture reaches pH 4.0 and the heat of ammoniation maintains the temperature of 180°C. The ammoniated product may be flaked and crushed to give a product with an N:P ratio of 2.4:1, which may be blended with potassium chloride to give a 24:10:10 compound fertilizer.

In another process phosphoric acid,

ammonium nitrate and ammonia are introduced into the mixing tank but no recycled material from the drying tower. The heat of reaction causes the mixture to boil at 155°C, the steam being scrubbed prior to venting. Thus a considerable part of the moisture is removed and the melt is then pumped into the drying tower, fitted with steam tubes where the drying process is completed in a counter current of hot air at 165°C. At this stage the acidic melt has a pH of 2.5 and contains 0.8% moisture, and this is subsequently ammoniated to pH 4.0 at 160°C, a temperature which is maintained by recycling cooled producer fines. Granules obtained by this method have an N:P ratio of 2:1.

(*Phosphorous and Potassium*, No. 35, May/June (1968), 20)

Underproduction of Fertilizer at Rourkela

The steelwork at Rourkela is designed to produce 70,000 Nm^3 of coke oven gas per hour with 315 pushing/day and 320 Nm^3 of gas yield per tonne of dry coal charged, but the rated production has been never attained. The actual number of pushing varied between 204 and 246 and the gas yields 246-297 Nm^3/te of dry coal. Other unavoidable circumstances added to the under-rated output of the gas. Due to inadequate capacity of the existing scrubbers, CO_2 content in the supply gas increased from 1-9 to 3.0 per cent and H_2S also recorded a higher figure than desired. Acetylene was found to be present in quantity 3 to 5 times the specified limit. CO and N_2 concentrations in the actual supply were 7-8 and 4-9 against 6.8 and 4.8 per cent respectively. Unsaturates went up to 3.3 against predesigned value of 2.4 per cent, while methane ranged between 24 and 29 against 29 per cent originally scheduled. Instead of 59.2 per cent, the concentration of hydrogen was 48.5—56.0 per cent. The 3-stage screw compressor installed for delivering gas at 13 kg./cm^2 was not functioning.

The Central Fuel Research Institute, which carried out an investigation for the causes of underproduction, suggested improvement in hydrogen availability by increasing the gas output, which can be fulfilled by increasing the bulk density of the coke oven charge with the addition of about 0.5 per cent oil.

Another way of increasing the hydrogen concentration was by shift conversion technique, which would however necessitate installation of either additional CO_2 scrubbers or raising the capacity of the existing scrubbers to take the additional load of CO_2. Another advantage accruing out of it would be that the fractionation plant would function more efficiently as a result of the decreased CO load.

As the fertilizer plant was not designed to take the full load of increased gas production, improvement in gas purification system was considered essential for bringing down the concentrations of contaminants below the desired level. Incorporation of another H_2S purifier after the sodium carbonate washer in the by-product section was also suggested. Lower concentration of sulphur compound could help shift catalyst to maintain activity for a longer period.

(*FRI News*, **18** (1968), 26)

Coal Gasification

Today the aim of gasification does not stop at the technological development but to combat with its rivals, natural gas and LPG. The justification of a long range aim in coal gasification is based on: (i) coal is a low cost material compared to the field price of natural gas, (ii) it accounts for 65 per cent of the fossil fuel resources, 10 times larger than natural gas, (iii) coal is evenly distributed, and (iv) the science and technology have developed so as to furnish a significant base on which to build future technology.

6-7 years ago high Btu gas from coal was estimated to cost about $ 1.00/mm Btu. With known technology today the cost is estimated at 50-55 cents/mm Btu, and with developing technology the cost is estimated to go down by another 10-15 cents. The aim of the present day gasification programme should be to develop the process in such a manner that will produce a gas completely interchangeable with natural gas at a price competitive with or lower than natural gas delivered to be produced in the area.

(*Amer Gas Assn.*, **49** (3) (1967), 3, 15 and 31; Abstr. *FRI News*, **18** (1968), 31)

Ammonia Tanks

For the first time in India, the Eastern Railways' carriage and wagon workshop at Liluah near Calcutta has built ammonia tank wagons, which will also carry petroleum and gasoline.

(*Ind. Chem. J.*, **11** (11) (1968), 44d)

Effects on Yields of Potatoes of Three Amounts of NPK Fertilizer and the Residual Effects of Following Winter Wheat

Use of 15 cwt/acre of 13-13-20 fertilizer on heavy soils is justified for potatoes, providing it is broadcast. Working the fertilizer in to the soil is usually beneficial. At 5 and 10 cwt/acre placement of the fertilizer in bands 3 in. from the seed centre is better than broadcasting. Yields of green wheat grain and straw are increased by previous fertilizer applications, but not so much as by fresh fertilizer. Highwinter rainfall reduces the residual effects most, regardless of method of application. Green wheat contains slightly more, N, 1/5th less P and 2½ times more K than ripe grain and straw.

Effect of Nitrogen Fertilizers on Sulphur Nutrition of Crops

Increasing amount of mineral N increased mineralisation of organic S and uptake of S by winter wheat in a loam soil supplied with P and K but no S. In a sandy clay loam treated with superphosphate and K_2SO_4, mineral N decreased both mineralisation of soil organic S and uptake of S by flax.

Simon, Silvestre G., Chabannes J., Driard N. C.r. hebd.

Senac. Acad. Agr. Fr. 1967, 53, 691-697. Soils & Ferts. 1968, 31, (1), Feb. 495.

(*The World of NPKS*, No. 24, (1968) 30)

Bonemeal

The Indian Agricultural Research Institute, New Delhi has developed a process for the production of bonemeal. In the process, disintegration of bones is effected by the action of caustic soda and the paste obtained is cleaned using hydrochloric acid for removal of sodium hydroxide. The main raw materials are available indigeneously while no special plant or machinery is required.

(*Inf. News Letter, Indus. Liaison and Extn. Serv.*, **7** (2) (1968), 15.

Potassium Schoenite

A prototype potassium schoenite plant of the central Salt and Marine Chemicals Research Institute Bhavnagar, having 1.5 tons/day capacity, has been established at the Hindusthan Salt Works, Kharaghoda (Gujarat).

(*Inf. News Letter, Indus. Liaison and Extn. Serv*, **7** (2) (1968), 16)

Demand for Petroleum Products

The demand of petroleum products in India in 1975 is likely to be as follows ('000 tonnes): light distillate 7903, kerosene 4444, diesels 8404, heavy ends 6485,

bitumen 945, lubricants 896 and others 2929 (Total 32006). The approved processing capacity in the refinaries at present is 17.50 m. tonnes per year. The demand for the above products during 1975 is proposed to be met by increasing the refinery capacity by way of expanding the existing refineries or building new ones.

(*Oil Commentary*, **6** (3) (1968), 30)

Petrochemicals

The Union Cabinet has approved setting up of a petrochemicals corporation in the public sector with an initial authorised capital of Rs. 30/- crores. The corporation will implement the Gujarat aromatics project contracts for which were signed in May 1967 with an West German firm. It it will set up India's largest naphtha cracker plant adjacent to the aromatic near Baroda. The contracts for these are likely to be signed shortly.

Crude Oil in NEFA

The new exploratory well in the petroliferous belts in NEFA concession area spudded by Oil India Ltd. has already encountered very high pressure hydrocarbon, indicating either oil or gas. ONGC has also located similar belts in the Brahmaputra valley near Lakwa oilfield in Assam. A number of wells are to be drilled shortly by Oil India around Ningro village in NEFA. The two oil-bearing tracts when fully developed will not only help in narrowing down the wide gap between indigenous production of and total demand for crude oil to meet the established refinary capacity, but will also raise the north-eastern region's contribution to the country's oil economy ONGC, which began supply crude from its newest oilfields at Lakwa from early October, hopes to produce about 1.5 million tonnes of crude from Rudrasagar and Lakwafields together from 1971.

Technical Aid by FCI Ltd.

Planning & Development Division of FCI Ltd. has been selected by the State Fertilizer Manufacturing Corpr. of Ceylon to submit a tender for a fertilizer complex in Ceylon on a turn-key basis.

STATISTICS

TABLE 1—IMPORT OF PETROLEUM PRODUCTS IN INDIA DURING 1967

	'000 tonnes	Rs./crores	Countries from which Imported
Crude Oil	8703.3	79.59	Iran, Kuwait & Saudi Arabia
Light Distillates	60.1	2.59	Iran & Venezuela
Kerosene	484.4	9.99	USSR & Italy
Heavy Ends	28.2	0.30	Saudi Arabia
Lubricants	375.0	26.16	USA, UK, Netherlands, Yugoslavia & Thailand

[*Oil Commentary*, **6** (3) (1968), 31]

TABLE 2—PRODUCTION AND DISTRIBUTION OF N, P_2O_5 AND K_2O IN INDIA 1967-68 (APRIL-MARCH)

(Metric Tons)

Fertilizer	Production	N	P_2O_5	K_2O	Distribution	N	P_2O_5	K_2O
(1) Ammonium sulphate 20.6%	437,951	90,218	—	—	1,237,162	254,162	—	—
(2) Urea 46% N	214,982	98,894	—	—	987,056	454,046	—	—
(3) Ammonium sulphate nitrate 26%	61,384	15,960	—	—	88,459	22,999	—	—
(4) Calcium ammonium nitrate								
,, ,, 20.5%N	348,841	71,512	—	—	80,480	16,498	—	—
,, ,, 25.0%N	192,257	48,064	—	—	441,297	110,324	—	—
,, ,, 26.0%N	—	—	—	—	—	—	—	—
,, ,, 22.0%N	—	—	—	—	—	—	—	—
(5) Ammonium chloride 25%N	15,475	3,869	—	—	43,125	10,781	—	—
(6) Ammonium phosphate sulphate (16-20-0)	92,401	14,784	18,480	—	88,748	14,200	17,750	—
(7) Diammonium phosphate (20-48-0)	27,714	5,543	13,303	—	22,027	4,405	10,573	—
,, ,, (18-46-0)	—	—	—	—	455,368	81,966	209,469	—
(8) Nitrophosphate (16-13-0)	22,355	3,577	2,906	—	35,350	5,656	4,596	—
,, (20-20-0)	70,457	14,091	14,091	—	37,257	7,451	7,451	—
,, (15-15-7.5)	700	105	105	53	630	95	95	47
,, (18-18-9)	602	108	108	54	391	70	70	35
(9) Urea ammonium phosphate (28-28-0)	5,189	1,453	1,453	—	5,189	1,453	1,453	—
(10) Ammonium phosphate (20-20-0)	—	—	—	—	209,382	41,876	41,876	—
(11) Basic slag (16% P_2O_5)	—	—	—	—	9,595	—	1,535	—
(12) N.P.K. Mixture (14-14-14)	—	—	—	—	83,371	11,672	11,672	11,672
(13) Superphosphate 16% P_2O_5	862,419	—	137,987	—	755,772	—	120,924	—
17.5% P_2O_5	4,465	—	781	—	572	—	100	—
18% P_2O_5	18,373	—	3,307	—	14,402	—	2,592	—
18.5% P_2O_5	45	—	8	—	1,283	—	237	—
19% P_2O_5	4,054	—	707	—	418	—	79	—
21% P_2O_5	349	—	73	—	—	—	—	—
17% P_2O_5	1,674	—	285	—	—	—	—	—
(14) Muriate of potash 60% K_2O	—	—	—	—	295,607	—	—	177,365
50% K_2O	—	—	—	—	5,816	—	—	2,908
(15) Sulphate of potash 50% K_2O	—	—	—	—	16,442	—	—	8,221
Total		368,178	193,657	107		1,038,347	430,472	200,248

[Fertilizer News, Sept. (1968)]

TABLE 3—ANNUAL DISTRIBUTION OF STRAIGHT NITROGENOUS FERTILIZERS
1967-68 (July-June)

Distributed to	Ammonium sulphate	Urea	Ammonium sulphate nitrate	Calcium ammonium nitrate 20.5% N	Calcium ammonium nitrate 25% N	Calcium ammonium nitrate 26% N	Ammonium chloride	Total 'N' Distributed
South	**537,441**	**447,004**	**35,605**	**40,555**	**704**	**58,150**	**19,720**	**354,498**
Andhra Pradesh	176,377	176,488	16,589	22,441	—	16,951	10,867	134,107
Kerala	43,397	26,690	120	1,902	—	—	—	21,181
Madras	166,691	158,529	4,611	275	—	20,608	2,208	114,826
Mysore	103,206	79,673	6,263	6,146	—	18,185	6,645	67,267
Pondicherry	4,250	1,430	—	—	—	—	—	1,530
U.P.A.S.I.	25,075	1,203	414	2,361	—	—	—	6,295
Coffee Board	11,002	2,918	7,201	7,430	—	2,406	—	7,628
Rubber Board	6,644	73	407	—	—	—	—	1,504
Cardamom Board	799	—	—	—	—	—	—	169
West	**223,910**	**220,944**	**9,700**	**14,234**	**—**	**11,457**	**9,790**	**158,310**
Gujarat	56,534	86,065	298	—	—	7,222	293	52,912
Madhya Pradesh	39,332	30,038	—	—	—	—	9,497	24,297
Maharashtra	125,429	104,668	9,402	14,284	—	4,235	—	80,483
Goa	2,573	125	—	—	—	—	—	588
Dadra Nagar Haveli	42	48	—	—	—	—	—	30
North	**333,277**	**309,506**	**35,522**	**93,120**	**264,672**	**46,409**	**15,728**	**321,411**
Haryana	20,277	26,827	—	16,532	61,947	5,039	—	36,692
Jammu & Kashmir	23,919	2,784	—	3,463	4,457	408	—	8,140
Punjab	101,707	47,355	7,991	31,178	147,619	17,768	—	92,545
Rajasthan	17,762	27,936	—	3,162	15,796	5,779	—	22,873
Uttar Pradesh	167,418	203,107	27,531	37,381	22,294	13,827	15,728	155,649
Delhi	221	225	—	770	5,100	—	—	1,594
Himachal Pradesh	1,973	984	—	634	7,459	3,588	—	3,786
Chandigarh	—	288	—	—	—	—	—	132
East	**272,334**	**101,399**	**3,165**	**58,700**	**154**	**14,255**	**12,812**	**122,489**
Assam	—	869	—	—	—		—	400
Bihar	114,553	55,878	2,693	5,451	—	14,255	9,973	57,311
Orissa	132	626	—	49,367	154	—	—	10,563
West Bengal	75,093	42,447	472	2,419	—	—	2,839	39,269
Manipur	576	1,213	—	—	—	—	—	671
Tripura	—	94	—	479	—	—	—	141
Nagaland	—	—	—	—	—	—	—	—
Andamans	—	—	—	—	—	—	—	—
Dandakaranya	96	96	—	484	—	—	—	163
Tea (NE)	81,884	176	—	—	—	—	—	16,971
Others	6,252	443	2	—	—	—	3,255	2,305
Total	1,373,241	1,079,296	83,994	247,672	265,530	130,271	61,305	959,014
Nepal	2,905	—	—	—	—	—	—	598
Grand Total	1,376,119	1,079,296	83,994	247,672	265,520	130,271	61,305	959,612

[*FAI Inf. Serv.*, 9 (20) (1968)]

TABLE 4—CONSUMPTION OF FERTILIZERS PER UNIT AREA OF AGRICULTURAL LAND IN INDIA 1967-68

Zone/State	Consumption in kg per hectare			
	N	P_2O_5	K_2O	Total
South	**11.64**	**4.68**	**2.42**	**18.74**
Andhra Pradesh	11.23	3.57	0.29	15.09
Kerala	9.55	4.29	7.32	21.16
Madras	19.05	8.46	5.74	33.25
Mysore	6.76	3.65	1.66	12.07
Pondicherry	38.35	18.00	8.63	64.98
West	**3.42**	**1.75**	**0.51**	**5.68**
Gujarat	5.33	2.70	0.27	8.30
Madhya Pradesh	1.07	0.36	0.15	1.58
Maharashtra	4.97	2.68	1.04	8.69
Goa	8.10	5.59	2.13	15.82
North	**6.84**	**2.22**	**1.24**	**10.30**
Jammu & Kashmir	11.58	11.55	9.06	32.19
Punjab*	13.82	3.64	1.03	18.49
Rajasthan	1.43	0.44	0.07	1.94
Uttar Pradesh	7.91	2.55	1.96	12.42
Delhi	23.97	9.50	—	33.47
Himachal Pradesh	2.39	1.19	0.11	3.69
East	**4.27**	**1.28**	**0.58**	**6.13**
Assam	0.12	0.48	0.22	0.82
Bihar	5.79	2.35	0.27	8.41
Orissa	1.28	0.19	0.25	1.72
West Bengal	5.40	1.39	1.74	8.53
Manipur	3.71	1.58	—	5.29
Tripura	0.30	0.16	—	0.46
Nagaland	—	0.08	—	0.08
Andamans				
All-India	6.40	2.47	1.16	10.03

*For the erstwhile State of Punjab.

Calculated on the basis of distribution figures.

[*FAI Inf. Serv.* **9** (22) (1968), 9]

TABLE 5—IMPORT OF PESTICIDES IN INDIA

Item	1965-66		1966-67		1967-68		Remarks
	Qty. kg.	Value, Rs. (thousand)	Qty, kg.	Value, Rs. (thousand)	Qty, kg.	Value, Rs. (thousand)	
1. Aldrin	79,545	6,71	1,60,989	22,56	3,52,227	52,17	
2. Aluminium Phosphide	10,000	3,55	40,025	22,41	99,993	5,58	Excel
3. BHC	6,71,801	13,82	6,98,600	8,83	94,000	1,21	More units licenced
4. Chloro Benzilate	3,992	1,08	3,000	1,28	998	37	
5. Chlordane	16,646	1,09	84,469	7,54	28,867	2,80	Mysore Fertilizers
6. DDT	72,81,460	1,42,64	12,69,914	46,66	36,79,568	1,20,26	More Units. Hindustan Insecticides, Alwaye
6a. DDT Propr.	9,63,737	9,93	376	1	5,25,001	17,40	
7. DDVP	No import		5,000	1,75	30,683	10,46	
8. Dieldrin	19,341	3,37	30,145	7,06	47,502	10,70	
9. Endrin	3,76,222	86,54	5,49,196	2,02,02	5,90,614	2,28,28	Mysore Fertilizers. Shell International
10. Heptachlor	13,521	99	1,17,658	13,13	40,461	4,49	Mysore Fertilizers
11. Lindane	79,430	8,65	3,40,724	66,06	13,380	2,71	Tata Fisons, pesticides
12. Parathion Ethyl	1,58,774	10,19	91,912	8,94	1,63,321	16,40	Bayer, Agrochem. Ltd.,
13. Parathion Methyl	60,760	4,67	53,000	5,80	1,36,360	15,27	Cynamid, pesticides
14. Parathion others	19,73,884	94,74	46,63,471	3,78,51	10,05,235	95,03	
15. Pesticides NES	54,472	6,58	1,31,009	21,43	3,44,424	19,03	
16. Other Weedicides	14,785	93	9,499	2,08	2,607	73	Argomore, Atul. Pesticides Ltd.,
17. Zineb	40,281	1,34	77,323	3,09	96,791	5,03	Fungicide. Bayer (letter of intent).
18. Others	1,55,246	14,98	83,673	8,05	13 226	64	Details

[*Indian Chem. J.*, **3** (3) (1968), 25 (Blue page)]

TABLE 6—IMPORT OF CHEMICALS IN INDIA

Value in Rs. crores

Item	1965-66	1966-67	1967-68
Fertilizers	44.8	97.3	142 7
Pesticides	4.1	8.3	6.1
Organic Chemicals	20.7	38.8	60.8
Inorganic Chemicals	16.5	13.7	17.7
Drug & Pharmaceuticals	8.3	16.2	13.1
Resins	5.6	7.3	6.1
Miscellaneous (+Rubber)	37.30	37.17	20.10
Dyes	3.3	3.8	3.7
Sulphur	6.93	11.71	36.79
Non-ferrous metals	67.2	83.5	86.6
Synthetic Fibres	1.9	0.96	1.1

[*Indian Chem. J.*, 3 (3) (1968), 32 (Blue page)]

TABLE 7—ANTICIPATED GROWTH IN POPULATION, ESTIMATED FOODGRAINS REQUIREMENTS AT 18 OZ/PERSON/DAY AND THE CORRESPONDING FERTILIZER REQUIREMENTS IN INDIA

Year	Population(1) (million)	Foodgrain(2) requirement (million tonnes)	Additional grain needs during each year (million tonnes)	Nutrient output ratio	Additional plant nutrient requirements for producing the additional grain during each year (million tonnes)	Total plant nutrient requirements for foodgrain production during each year (million tonnes)
1969-70	541	121.0	−3.6(3)	8.9	−0.40(3)	2.50
1970-71	555	124.6	—	9.9	—	2.90
1971-72	569	128.1	3.5	11.0	0.32	3.22
1972-73	583	131.7	3.6	12.2	0.30	3.52
1973-74	598	135.5	3.8	13.5	0.28	3.80

(1) 2.5% over the 1970-71 level of 555 million
(2) Includes buffer stock, feed, seed and wastage.
(3) Less in relation to the 1970-71 level.

[*Report on the Development of Fertilizer Industry during IV Plan*, (Fertilizer Assn. of India, New Delhi), 1968, 37]

TABLE 8—YEARWISE ESTIMATED FOODGRAIN PRODUCTION AND FERTILIZER REQUIREMENTS IN INDIA

Year	Grain yield(1) (million tonnes)	Increase in yield during each year (million tonnes)	Nutrient/ output ratio	Additional fertilizer nutrient required in each year (million tonnes)	Fertilizer requirements for foodgrains production in each year (million tonnes)	Total fertiliser(2) requirements (million tonnes)	N (In the proportion of 4:2:1)	P_2O_5	K_2O
1967-68	98	—	8.0	—	1.20	1.70	0.97	0.49	0.24
1968-69	102.9	4.9	8.4	0.58	1.78	2.52	1.44	0.72	0.36
1969-70	108.0	5.1	8.9	0.57	2.35	3.32	1.90	0.95	0.47
1970-71	113.4	5.4	9.9	0.55	2.90	4.10	2.34	1.17	0.59
1971-72	119.1	5.7	11.0	0.52	3.42	4.84	2.77	1.38	0.69
1972-73	125.1	6.0	12.2	0.49	3.91	5.53	3.16	1.58	0.79
1973-74	131.4	6.3	13.5	0.47	4.38	6.19	3.54	1.77	0.88

(1) Calculated assuming 5% rate of increase annually over the 1967-68 estimate of 98 million tonnes.
(2) Calculated assuming consumption between food and non-food crops to be in the proportion of 2.9 : 1.2.

[*Report on the Development of Fertilizer Industry, during IV Plan*, (Fertilizer Assn. of India, New Delhi), 1968, 46]

CORRIGENDA

TECHNOLOGY, Vol. 5, No. 2, 1968, p. 89, paper entitled "Stress-Corrosion Cracking of 18-8 Cr-Ni Stainless Steels in Ammonium Sulphate Vessels" by C. Aravindakshan, Ajit Roy and B. K. Banerjee.

Table 4, under the column F_{c_3} for Austenite Phase, Sl. No. 2:

please read 10.9 *instead of* 16.9

TECHNOLOGY, Vol. 5, No. 3, 1968, paper entitled "Temperature Co-efficient of Kovats Retention Index as a New Parameter in the Identification of Gas Chromatographic Peaks" by N. C. Saha and G. D. Mitra.

page 215 Fig. 4A *please read* 3 MH *for* 2 MH in the 8th line from top

page 215 Fig. 4C *please read* 740 *for* 240 along the ordinate

page 217 Tables 1B & 2 *please read* $\frac{dI/dt \times 10^3}{n}$ in *for* $\frac{dI/dt \times 10^3 \text{ in}}{n}$

page 216 Line 5 *please read* Trialkyl *for* Trialky

TECHNOLOGY, Vol. 5. No. 3, 1968, paper entitled "Salt-Coated Silica Gel Supports in the Gas Chromatography of Saturated Hydrocarbons" by Samir K. Ghosh and N. C. Saha.

page	226	line	4	*please read*	Fig.	4A	*for.* Fig.	3A
page	226	line	5	*please read*	Fig.	4B	*for* Fig.	3B
page	226	line	24	*please read*	Fig.	3A	*for* Fig.	4A
page	226	line	25	*please read*	Fig.	3B	*for* Fig.	4B
page	226	line	39	*please read*	Fig.	3A	*for* Fig.	4A
page	227	Fig.	4A	*please read*	2, 3, 4	TMP	*for* 2, 3, 4	TMH